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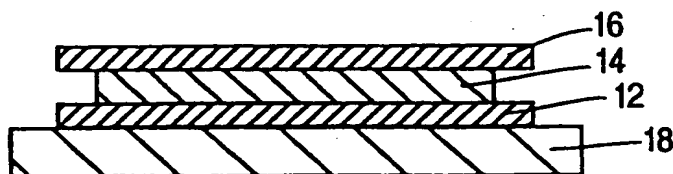
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(54) Title: ELECTROLUMINESCENT DIODES UTILIZING BLENDS OF POLYMERS

(57) Abstract

Blends of luminescent polymer in a matrix of hole transporting polymer serve as active layers (14) in LEDs (10). The use of polymer blends reduces the amount of costly luminescent polymer employed, leads to higher efficiencies and causes wavelength shifts in the emitted light as compared to homopolymer based active layers. The color shift allows color tuning and permits high efficiency blue LEDs to be obtained. Methods for forming the blends and methods for using them in LEDs (10) are also disclosed.



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ELECTROLUMINESCENT DIODES UTILIZING  
BLENDS OF POLYMERS

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Field of the Invention

This invention is in the field of light-emitting diodes and their fabrication. More particularly, it concerns improvements in light emitting diodes based on semiconducting  $\pi$ -conjugated organic polymers.

Background Information

Solid-state light emitting diodes (LEDs) have found widespread application in displays, as well as in a variety of less common applications. Currently, commercial LEDs are fabricated with active layers fabricated from inorganic semiconductors; for example, gallium arsenide (GaAs), typically doped with aluminum, indium, or phosphorus. Using this technology, it is very difficult to make large area displays. In addition, the LEDs made of these materials are typically limited to the emission of light at the long wavelength end of the visible spectrum.

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For these reasons, there has been considerable interest for many years in the development of suitable organic materials for use as the active (light-emitting) components of LEDs.

5  $\pi$ -conjugated polymers have been identified as materials for this application. These polymers offer in single materials the properties of conducting electricity (i.e. being semiconductive) and of being luminescent. As such they offer a number of advantages over conventional  
10 inorganic semiconductors for light-emitting diode (LED) applications. The ability to alter the  $\pi$ - $\pi^*$  energy gap through controlled changes in the molecular structure offers promise of providing colors which span the visible spectrum. Some of these materials may be fabricated into  
15 LED structures by casting from solution which is a significant manufacturing advantage (United States Patent application serial number 07/66290 of Braun and Heeger; Gustafsson, G. et al., Nature (1992) 357:477; and Braun, D. et al., J. Appl. Phys. Lett. (1992) 61:3092 ). These  
20 materials also permit LEDs to be constructed on flexible substrates and thus promises to enable the fabrication of novel light sources and displays in a variety of unusual shapes.

Initial results from such polymer LEDs have  
25 shown that a wide variety of colors can be realized with impressive efficiency, brightness, and uniformity (Burn, P.L. et al., Chem. Commun. (1992) 32; Burn, P.L. et al., Nature (1992) 356:47; Burroughes, J.H. et al., Nature (1990) 347:539; Brown, A.R. et al., Appl. Phys. Lett. (1992) 61:2793; Grem, G. et al., Adv. Mater (1992) 4:36;  
30 Ohmori, Y. et al., Jpn J. Appl. Phys. (1991) 30:L1941; Ohmori, Y. et al., Solid State Commun. (1991) 80:605; Ohmori, Y. et al., Jpn. J. Appl. Phys. (1992) 31:L568; Braun, D. et al., J. Appl. Phys. (1992) 72:564; Braun, D.

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et al., J. Appl. Phys. Lett. (1991) 58:1982; and Yang, Z. et al., Macromolecules (1993) 26:1188).

Although there has been rapid progress in research on polymer LEDs, the number of polymers which offer both proper levels of conductivity and relatively high luminescence efficiency is limited; the principal examples being poly(2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV) (Wudl, F. et al., Materials for Nonlinear Optics: Chemical Perspectives (Marder, S.R. et al. eds.) American Chemical Society Symposium Series, Vol. 455 (1991) p. 683-686), and poly(2-5-bis(cholestanoxyl)-1,4-phenylene vinylene) (BCHA-PPV) (Wudl, F. et al., J. Polym. Preprints (1993) 34:197). Both MEH-PPV and BCHA-PPV are soluble in the conjugated form in common organic solvents. LEDs fabricated with MEH-PPV emit orange light; LEDs fabricated with BCHA-PPV emit yellow light (Zhang, C. et al., J. Electron. Mat. (1993) in press). While these materials offer promise, they often are expensive and present less than optimal mechanical properties.

One alternative to these materials which has been proposed is to mix fluorescent dyes or other discrete monomeric small molecule luminescent species into a conductive polymer to achieve an active layer material. This approach has the disadvantages of likely incompatibility between the small molecules and the polymer structure and of limited application of the products to environments where the small units are not gradually extracted from the polymer.

Recently, Martelock et al., Makromol. Chem. (1991) 192:967, reported the synthesis of poly(p-phenylphenylene vinylene) (PPPV) using a Heck reaction from ethylene and 2,5-dibromobiphenyl. Vestweber, H. et al., Adv. Mater. (1992) 4:661, fabricated green LEDs using this material as the active electroluminescent

## STATEMENT OF THE INVENTION

Thus, in one aspect, this invention provides new materials useful as the active layer in light emitting diodes. These new materials are light emitting polymer compositions which include

- in intimate blended admixture.
- These blended materials offer the desired electroluminescence and conductivity properties as well as the potential for superior physical properties, as compared to organic luminescent materials of the past. In addition, we have found that the amount of expensive luminescent (i.e. emitter) polymer can be reduced to very low levels in these blends, if desired. At these low levels cost benefits are achieved and the efficiency of the luminescent polymer actually increases. We have also found that the use of separate luminescent and hole transporting polymers can shift the wavelength of the

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light emitted by the luminescent material. This property can be used to "tune" the color of the light emitted by the luminescent polymer so as to obtain blues and other previously difficult to achieve colors. One can also use  
5 this property to move the emission out of the infrared into the visible spectrum.

In another aspect this invention provides improved light emitting diodes. These diodes are made up of

10 a transparent conducting first layer having a high work function and serving as a ohmic hole injecting electrode,

a film of light-producing conjugated polymer present upon the conducting first layer, and

15 a negative, electron injecting contact formed from a low work function metal and present upon the film of light producing conjugated polymer so as to act as a rectifying contact in the diode structure. In these diodes the improvement involves employing as the film of  
20 light-producing conjugated polymer a film of a polymer composition which includes

a) a hole transporting polymer and  
b) a polymeric conjugated organic emitter  
having at least two mer units

25 in intimate blended admixture.

In other aspects this invention provides methods for forming these conductive materials by blending the hole transporting polymer and the polymeric conjugated polymer emitter. In addition it provides  
30 methods for forming LEDs in which the blend so formed is cast into a film upon a preformed ohmic hole injecting layer or a preformed negative electron injecting contact layer. Alternatively, in accord with the invention, the film of the blended polymers can be preformed and the  
35 other necessary layers applied to it. Casting solutions

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of the blends of hole transporting polymer and polymeric conjugated emitter with a suitable mutual solvent are also provided.

## DETAILED DESCRIPTION OF THE INVENTION

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### Brief Description of the Drawings

This invention will be further described with reference being made to the accompanying drawings. In these drawings

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Figs. 1A, 1B show the structures of a representative light-emitting polymer, poly(p-phenylphenylene vinylene) (PPPV) and a representative conductive polymer poly(9-vinylcarbazole) (PVK) which can be blended to practice the present invention.

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Fig. 2 is a series of graphs depicting absorption spectra (films on glass) for (a) PPPV, (b) PVK and (c) PPPV/PVK blends (1/10).

20

Figs. 3A, 3B are graphs illustrating the dependence of current on applied voltage (A) and emission intensity on applied voltage (B) for PPPV/PVK (1/50) blend LEDs.

Fig. 4 is a graph illustrating dependence of electroluminescence efficiency on the PPPV/PVK ratio.

25

Fig. 5 is a graph showing emitted light intensity and device current (Ca/Blend/ITO) for different PPPV/PVK ratios.

Fig. 6 is a graph showing electroluminescence efficiencies vs. current for LEDs with different PPPV/PVK ratios.

30

Fig. 7 is a graph showing the electroluminescence (solid line) and photoluminescence (dashed line) from a PPPV/PVK (1/50) blend measured at room temperature.

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Fig. 8 is a graph showing the photoluminescence of PVK, PPPV/PVK blends and PPPV films at room temperatures.



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Fig. 9 is a graph showing electroluminescence spectra of PPPV/PVK blend LEDs (Ca/Polymer Film/ITO) for different PPPV/PVK ratios.

Fig. 10 is a schematic cross-section of a light emitting diode of this invention.

#### Description of Preferred Embodiments

The present invention calls for blends of a hole transporting polymer with a luminescent conjugated polymer. The luminescent polymer is also referred to as the emitter or the emitter polymer. These blends function as an active layer in light emitting diodes.

As used herein a "polymer" is defined to be a material which has a plurality, i.e. two or more (usually identical) repeat units covalently bonded to one another. A separate repeat unit is referred to as a "mer" unit so that a "polymer" will have at least two mer units and preferably, to achieve desired polymer properties, at least about five mer units. Included are polymers having two or more different kinds of mer units, i.e. copolymers. "Polymers" are to be distinguished from monomers or other discrete chemical molecules which contain but a single intact unit.

#### The Hole Transporting Polymer

The hole transporting polymer used in the blends of this invention is typically selected from polymers (most commonly organic polymers but in a few cases silicon-based polymers) which have a saturated backbone with conjugated groups pending from it or which have a backbone which includes a series of separate conjugated groups, typically a series of conjugated regions isolated from one another by nonconjugated regions. "Hole transport" occurs when the holes hop from one pendant or isolated conjugated group to the next.

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This mode of transport is distinguishable from the type of conductivity observed with electron transporting polymers. In electron transport continuous conjugated backbone which serves as the conductive medium.

5           These types of hole transporting polymers include, without limitation, nonconjugated organic polymers having depending optionally N-substituted carbazole units or aromatic amines as the hole transporting species, silicone containing polymers with  
10 carbazole or aryl groups as depending substituents as the hole transporting species and polycarbonate materials wherein the carbonate groups serve as conjugation blocks separating discrete conjugated aromatic and/or olefinic regions which are themselves capable of carrying holes.

15           Representative examples of these materials include the following species:

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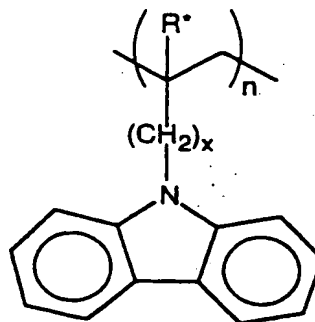
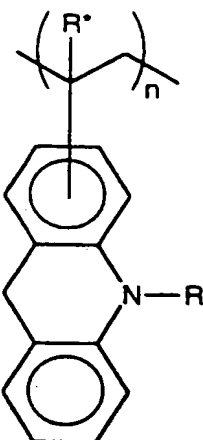
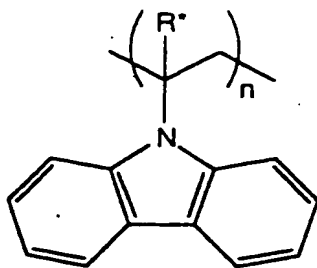
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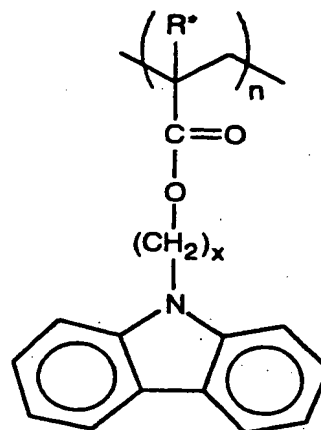
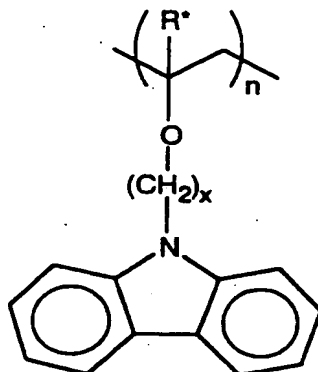
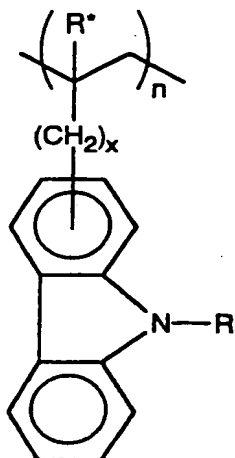
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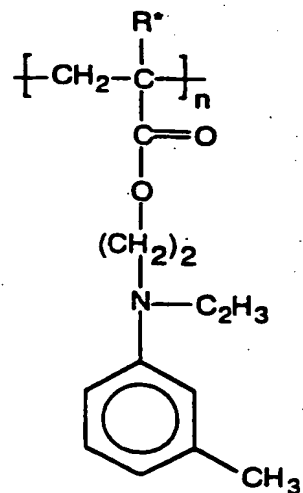
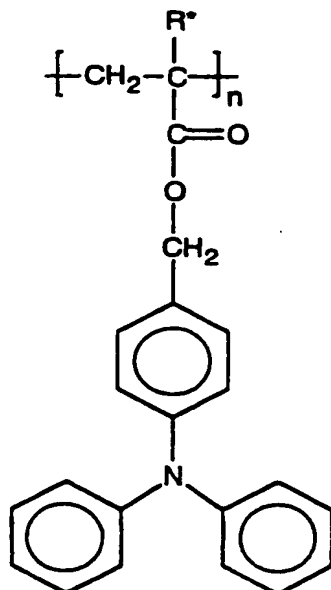
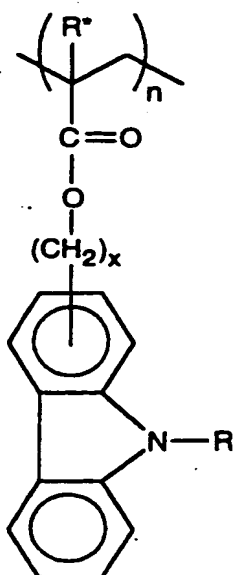
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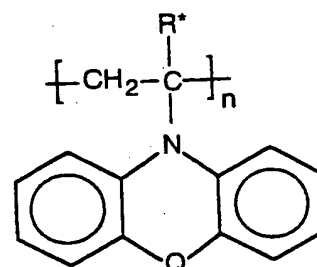
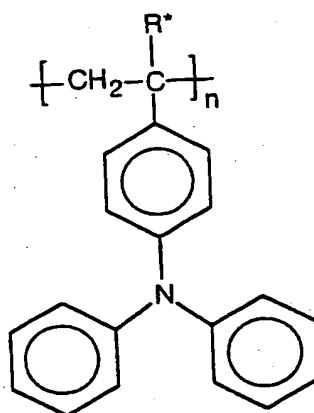
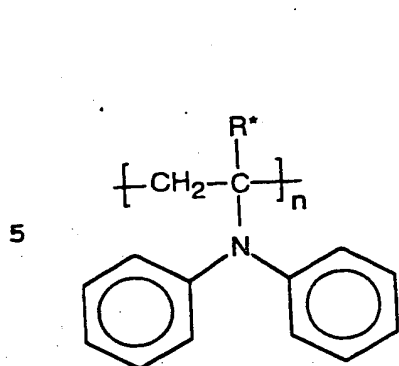


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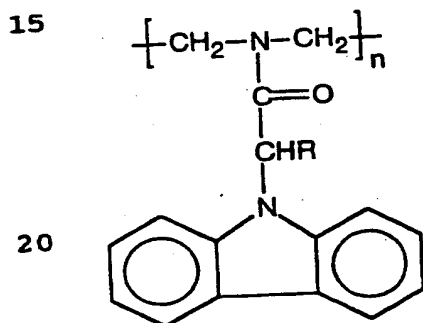
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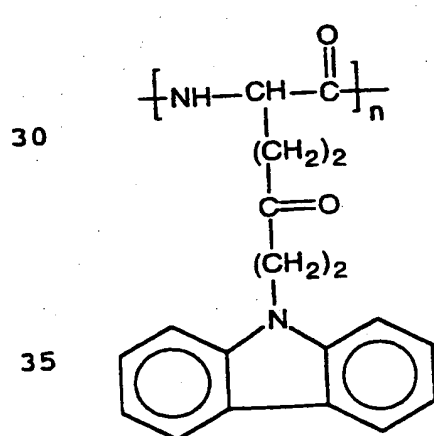


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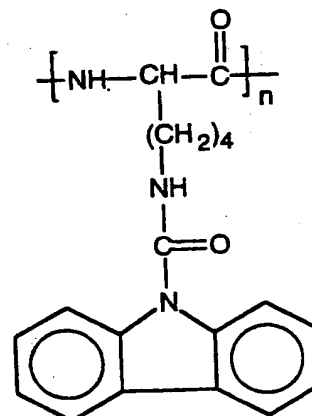
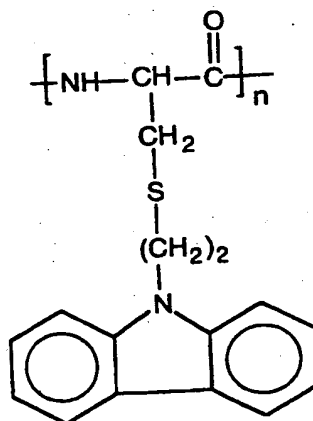


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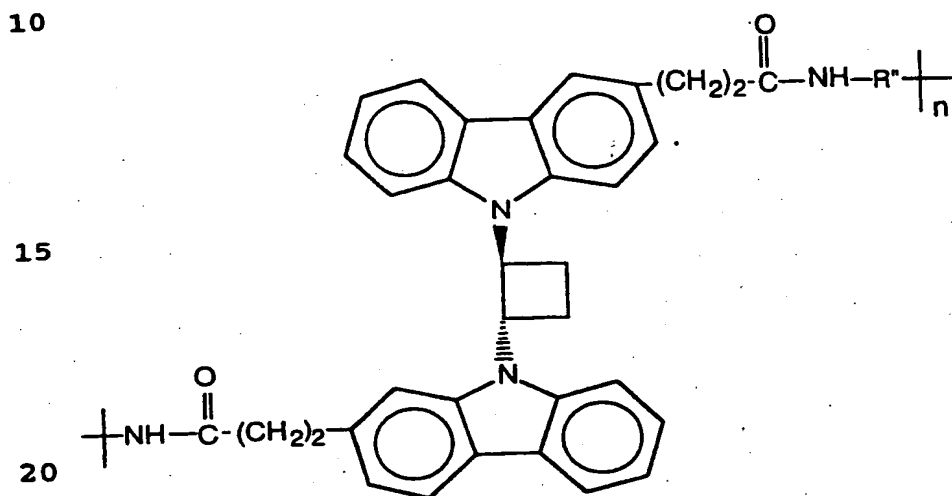
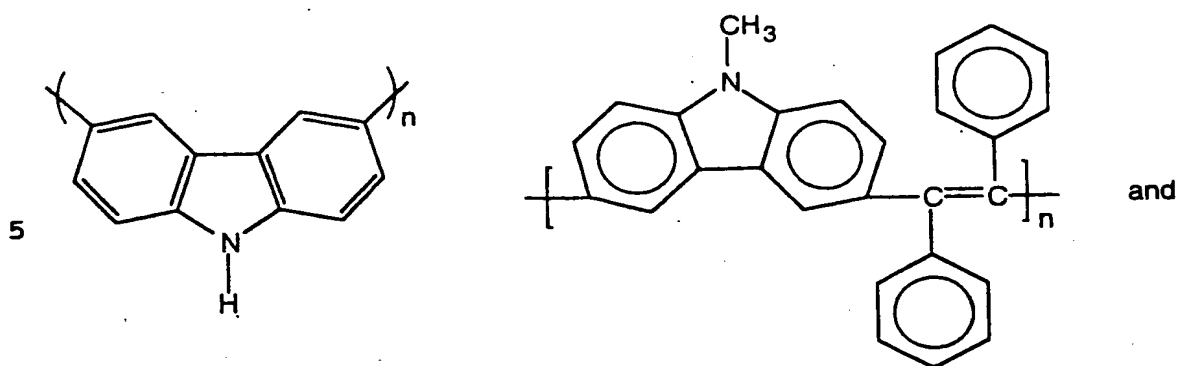
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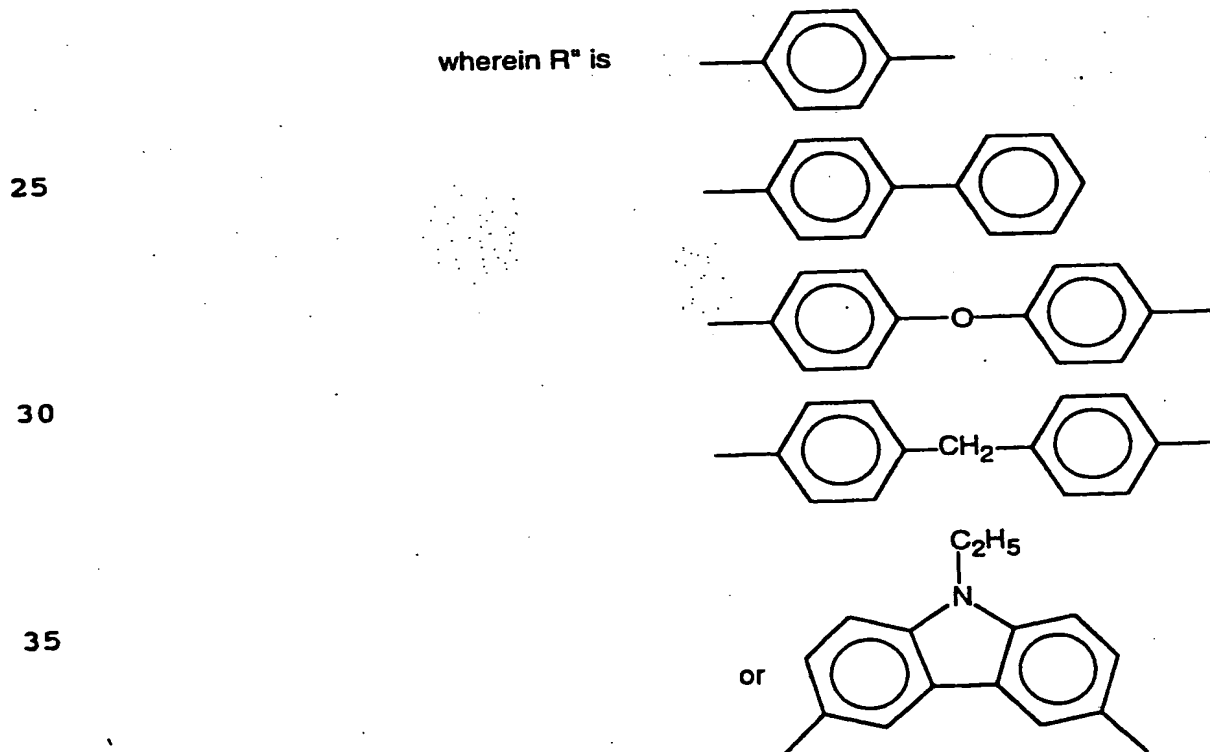
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wherein R\* is

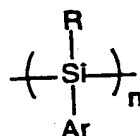
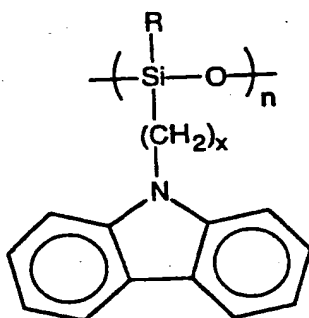


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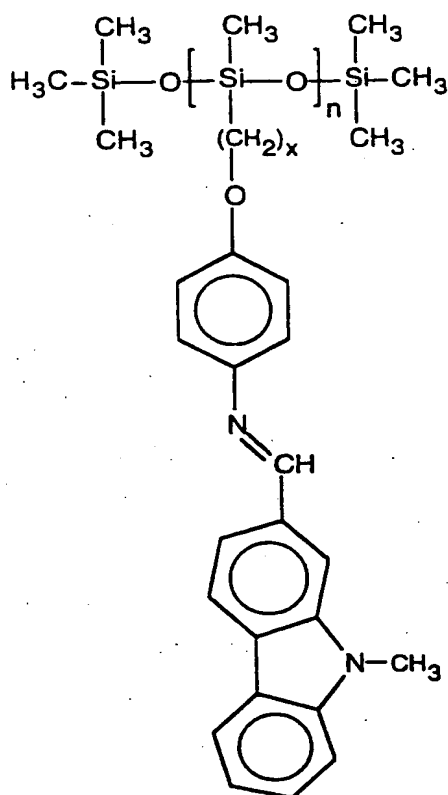
In these formulae, and the other hole transporter formulae  $n$  is an integer representing the number of new units in the polymer  $n$  is greater than 1, preferably from about 2 to about 5000, especially from about 10 to about 4000. These values give rise to a molecular weight for the hole transporter of from about 1 kD to as much as 500 kD or greater.

It should also be noted that these formulae imply an "ethylene" homopolymer. In fact, the backbone units may be organic groups other than "ethylene" capable of supporting pendant carbazole units, and the backbone may include amounts of other copolymerized hole transporting or noninterfering groups. At this time however we prefer to use simple hole transporting polymers. In these structures  $x$  is an integer ranging from 1 to about 16, especially 1 to 8;  $x'$  is an integer ranging from 1 to about 8, especially 1;  $R$  is an alkyl (linear, branched or cyclic) having from 1 to about 12 carbons and especially from 1 to 8 carbons such as methyl, ethyl, *n*-propyl, isopropyl, the butyls, pentyls, hexyls and the like.  $R^*$  is hydrogen or an alkyl, like  $R$ , preferably hydrogen or methyl.  $Q$  is S or O.

Other representative hole transporting polymers include the following materials possessing silicon containing backbones (eg. polysiloxanes, polysilanes):



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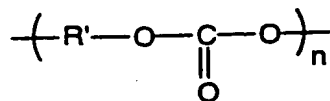
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20 In these polymers  $n$ ,  $x$  and  $R$  have the meanings  
 set forth above. The silicon-containing backbone is not  
 conjugated. The pendant groups provide whole transport.  
 In the case of the polysiloxanes,  $R$  is most preferably  
 methyl.  $\text{Ar}$  is an aromatic group of from about 6 to about  
 12 carbons such as an aryl (phenyl), an alkaryl, or an  
 25 arylalkylene. Phenyl is the presently preferred  $\text{Ar}$   
 group.

Another family of representative hole  
 transporters is the polycarbonates wherein the several  
 carbonate linkages separate and isolate individual  
 30 localized conjugated regions of a polymer backbone.  
 These materials are represented generically by the  
 formula

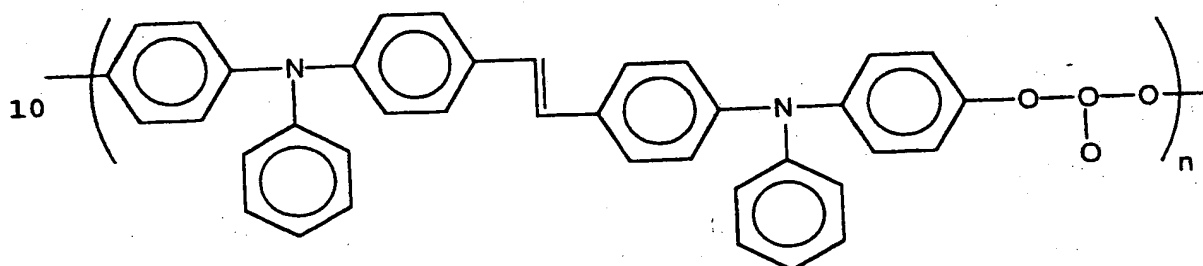


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wherein R1 is a conjugated organic group such as a group including conjugated olefinic bonds or conjugated aromatic rings, and n is as defined above.

A representative example of this class of materials has conjugated triarylamine units as the isolated hole transporters and presents the following structure, in which n has the meaning previously given:



15 Other hole transporting polymers may be used. Similarly, mixtures of two or more hole transporting polymers may be used. Polymers having two or more transporting moieties may be used.

At this time, poly(9-vinylcarbazole) is the most preferred hole transporting polymer.

20 These hole transporting polymers and their preparation have been described in the literature. Many, such as the preferred PVK material, are available commercially as laboratory reagents. In addition, routes to substituted carbazoles are taught in the literature with the points of substitution being useful for incorporation into the polymers employed in these blends.

#### The Luminescent Polymer

30 The luminescent or emitter polymers used herein include conjugated organic polymers and especially  $\pi$  conjugated organic polymers known in the art. These include, for example, polyfluorenes of the formula



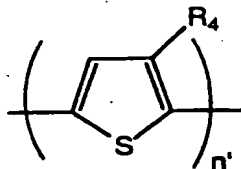


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In this structure,  $n'$  is an integer representing the number of mer units in the polymer.  $n'$  is at least 2 and preferably at least 3 and typically ranges from 2 to about 2000 and especially from about 5 or 10 to about 1000 so as to impart a molecular weight to the polymer of from about 1 kD to about 600 kD and especially 10 kD to about 500 kD.  $R_2$  and  $R_3$  are each independently selected from hydrogen and alkyls of from 1 to 12 carbon atoms and especially 1 to about 8 carbon atoms. As noted with reference to the hole conducting polymers, these formulae for the various representative luminescent polymers are to read expansively to include materials with less than full substitution and materials which contain minor amounts of noninterfering copolymerized units.

Another family of luminescent polymers which can be used are the poly(thiophenes). These materials include poly(thiophene) and poly(3-alkylthiophenes) and are represented by the formula

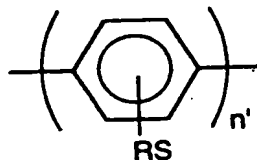
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In this formula  $n'$  is as defined above and  $R_4$  is hydrogen or an alkyl of from 1 to about 16 carbon atoms. Preferred materials have  $R_4$  as a 6 to 16 carbon atom alkyl.

Another representative family of luminescent polymers is the poly(p-phenylenes). These materials have the formula

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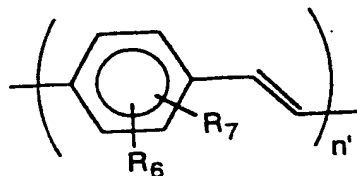
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wherein  $n'$  is as defined and  $R_5$  is hydrogen, an alkyl having from 1 to about 12 carbons and especially from 1 to 8 carbons, or an aromatic group of from about 6 to about 12 carbons such as an aryl (phenyl), an alkaryl, or an arylalkylene.

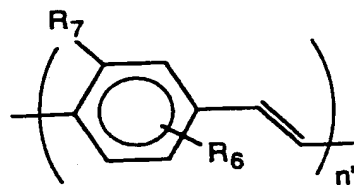
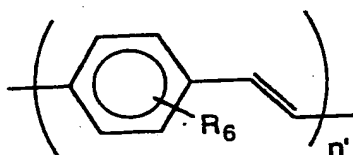
A further representative family of luminescent polymers is the poly(phenylene vinylenes) and in particular the poly(para-phenylene vinylenes). These materials have the formula

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wherein  $n'$  is as defined and  $R_6$  and  $R_7$  are each independently hydrogen, an alkyl having from 1 to about 12 carbons and especially from 1 to 8 carbons, an aromatic group of from about 6 to about 12 carbons such as an aryl (phenyl), an alkaryl, or an arylalkylene or an alkoxyl having from 1 to about 25 and especially 1 to about 20 carbon atoms. Among these materials the following general structures are preferred

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Poly(2,5-thienylenevinylenes) can also be used as the luminescent polymer.

Especially preferred materials are

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poly(p-phenylphenylene vinylene) ("PPPV"), poly(p-phenylene vinylene) ("PPV"), poly(2,5-dimethoxyphenylene vinylene) ("PDMPV"), poly(2-methoxy,5-ethylhexyloxyphenylene vinylene) ("MEH-PPV"), and poly(2-methoxy,5-(2'-ethyl-hexyloxy)-p-phenylene vinylene) ("PCHA-PPV"). Of these, the PPPV materials are preferred.

Mixtures of two or more luminescent polymers may be used if desired.

These representative luminescent polymers have been described in the art heretofore for use as conductive polymers. Their preparation is also described in the literature.

#### Optional Components of the Blend

As already noted, these polymer blends may contain materials in addition to a single luminescent polymer and a single hole transporter. Multiple materials may be used. In addition, minor amounts of inert or diluent materials may in theory be included without departing from the spirit of this invention. Any addition of other materials should be done with caution as they may interfere with the ability of the hole transporting polymer and the luminescent polymer to interact and yield desired high levels of light emission.

One important class of optional component to be considered is the electron transporting molecules or polymers. These materials are known in the LED field and are typically selected from oxadiazoles, and their derivatives. These materials, although not required, can make up as much as 50% of the total weight of the polymer blend.

#### Blend Proportions

One important advantage of the present invention is that it permits the amount of expensive

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luminescent polymer to be reduced. In the blends of this invention the weight ratio of hole transporting polymer to luminescent polymer is greater than 1:1 and preferably greater than 2:1 and typically ranges from about 2:1 to about 2000:1, and especially from about 5:1 to about 1000:1.

#### Blend Preparation and Solutions

The two components of this blend must be intimately admixed. This could be accomplished by melting the two polymers together. We have accomplished this intimate mixing by dissolving the two polymers in a mutual solvent. We prefer this method. In addition to permitting the desired intimate mixing, this use of mixing of solutions provides a convenient form of the blend for application into the final LED products.

The solvent or mixture of solvents employed should be selected so as to mutually dissolve both materials. Typically, common organic solvents are used. These can include halohydrocarbons such as methylene chloride, chloroform, and carbon tetrachloride, aromatic hydrocarbons such as xylene, benzene, toluene, other hydrocarbons such as decaline, and the like. Mixed solvents can be used, as well. Polar solvents such as water, acetone, acids and the like may be suitable. These are merely a representative exemplification and the solvent can be selected broadly from materials meeting the criteria set forth above.

Such a solution can be relatively dilute, such as from 0.1 to 30% w in concentration, particularly 0.1 to 30% w and especially 0.2 to 20% w.

#### Light Emitting Diode Structures

As shown in Fig. 10, the LED's provided by this invention (10) include, at minimum, an ohmic hole

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injecting electrode (12), a layer or film (14) of the polymer blend of this invention and an electron injecting rectifying contact (16). They may, in addition include a substrate or support (18) to provide physical robustness to the light emitting structure.

#### The Ohmic Hole-Injecting Electrode

The polymer blend layer of the LEDs of this invention is bounded on one surface by a transparent conducting first layer. This first layer is a transparent conductive layer made of a high work function material, that is a material with a work function above 4.5 eV. This layer can be a film of an electronegative metal such as gold or silver, with gold being the preferred member of that group. It can also be formed of a conductive metal-metal oxide mixture such as indium-tin oxide or of a conductive polymer such as poly(aniline) in the emeraldine salt form.

These layers are commonly deposited by vacuum sputtering (RF or Magnetron), electron beam evaporation, thermal vapor deposition, chemical deposition and the like.

The ohmic contact layer should be low resistance: preferably less than 300 ohms/square and more preferably less than 100 ohms/square.

#### The Electron Injecting Rectifying Contact

On the other side of the polymer blend film an electron-injecting contact is present. This is fabricated from a low work function metal or alloy. A low work function material has a work function below 4.3 eV. Typical materials include indium, aluminum, calcium, barium and magnesium and alloys thereof, with calcium being a particularly good material. These electrodes are applied by using methods well-known to the art (e.g.

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thermal evaporation, sputtering, or electron-beam evaporation) and act as the rectifying contact in the diode structure.

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### The Substrates

In some embodiments, the conjugated polymer blend-based LEDs are prepared on a substrate. The substrate should be transparent and nonconducting. It can be a rigid material such as a rigid plastic including rigid acrylates, carbonates, and the like, rigid inorganic oxides such as glass, quartz, sapphire, and the like. It can also be a flexible transparent organic polymer such as polyester - for example polyethyleneterephthalate, flexible polycarbonate, poly(methyl methacrylate), poly(styrene) and the like.

15

The thickness of this substrate is not critical.

### Additional layers

In addition to the required layers, one may also include a layer of the electron transporting molecule or polymer between the active layer and the electron injecting contact. This optional layer may be from 0 to 500 nm in thickness and is formed from the materials described above as electron transporting materials.

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### LED Fabrication

The polymer blends of this invention find application as active layers in LED's. These active layers are commonly present as films which are 5 to 1000 nm, and especially 10-500 nm in thickness, although thicker or thinner films and other configurations can be used if desired. The robustness and flexibility of the

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polymer blends are advantages when selecting configurations.

5 In one embodiment the polymer blend is cast into a free-standing film or body from solution. This casting step may employ spin casting, doktor blade casting or other techniques known in the art of polymer coating and film forming. The casting solvent can be the solvent used to prepare the blend, if desired. Solvent is removed and the film or body is coated on opposite  
10 sides with the hole injecting and electron injecting electrodes.

In another embodiment the polymer blend is cast onto a substrate on top of a previously deposited electrode layer. Then, after solvent removal, the other  
15 electrode layer is applied.

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Examples

This invention will be further described by the following examples. These are intended to embody the invention but  
5 not to limit its scope.

Example 1

In this example the use of a polymer blend as the active layer in an LED is demonstrated. The blend is  
10 composed of a soluble conjugated polymer poly(p-phenylphenylene vinylene) (PPPV), a soluble derivative of poly(p-phenylene vinylene) in a matrix of hole transporting polymer poly(9-vinylcarbazole) (PVK), a commercially available polymer. The molecular structures  
15 of poly(p-phenylphenylene vinylene) (PPPV) and poly(9-vinylcarbazole) (PVK) are shown in Figs. 1A, 1B. Both PPPV and PVK are soluble in common organic solvents.

This example describes the monomer synthesis, PPPV polymer synthesis and device fabrication, which is  
20 simplified because the blend can be spin-cast from a stable solution at room temperature. We present the results of electrical and optical characterization of the devices. The initial devices utilized calcium as the electron injecting (rectifying) contact and indium/tin-oxide (ITO) as the hole-injecting contact. The LEDs turn  
25 on at -30V and have a peak emission wavelength in the blue at 495 nm (at room temperature). The quantum efficiency was measured as a function of the PPPV content in the blend; the maximum efficiency was approximately  
30 0.16% photons/electron at a concentration of only 2% PPPV in PVK.

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PPPV was prepared by a polydehydrohalogenation reaction from 2,5-bis(bromomethyl)biphenyl (Scheme 1). This is a modification of a synthesis initially developed by Gilch, H.G. et al., J. Polym. Sci. Part A-1 (1966) 4:1337, and by Hörhold, H.-H. et al., J. Makromol. Chem. (1970) 131:105, to obtain the PPPV.



The monomer, 2,5-bis(bromomethyl)biphenyl (2), was prepared from 2,5-dimethylbiphenyl (1) (Land, H.T. et al., Makromol. Chem. (1990) 191:2005) via bromination with N-bromosuccinimide (NBS). The PPPV (3) was obtained from 2 by polydehydrohalogenation in the presence of potassium-t-butoxide in toluene under reflux. Catalytic amounts of 18-crown-6 ether were added to the reaction mixture. The PPV-formation started immediately after addition of the base and could be observed by the strong photoluminescence of the reaction mixture when irradiated with UV-light of  $\lambda = 365$  nm.

a. Monomer Synthesis - 2,5-Bis(bromomethyl)biphenyl (2):

A mixture of 6.70 g (37 mmol) of 2,5-dimethylbiphenyl (1) 14.00 g (78 mmol) of N-bromosuccinimide (NBS) and 10 mg (0.04 mmol) of

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dibenzoylperoxide in 100 mL of dry carbontetrachloride was heated to reflux for 15 h under argon atmosphere. A red solution with precipitated succinimide was obtained. The warm reaction mixture was filtered. The solid was extracted two times, each with 150 mL of hot hexane. The organic phases were combined, and the solvents evaporated. A pale yellow oil remained. The oil was cooled at -10°C overnight to yield a crystalline raw product. The product was recrystallized from hexanes (50 mL) to give white crystals. Yield: 6.0 g (48%) of 2. Purity, determined by GC: >99%, m.p. = 80°C, IR (KBr): 3020 (w; CH), 1438 (m, CH), 1215 (s), 780 (s), 700 (s), 651 (s). MS (70 eV):  $m/z$  340 ( $M^+$  of molecule containing one  $^{81}\text{Br}$  and one  $^{79}\text{Br}$ ), 261 ( $M^+ - ^{79}\text{Br}$ ), 259 ( $M^+ - ^{81}\text{Br}$ ), 179 ( $M^+ - 2 \text{ Br}$ ), 165 ( $M^+ - 2 \text{ Br} - \text{CH}_2$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 4.43 (s;  $\text{CH}_2$ ), 4.49 (s;  $\text{CH}_2$ ), 7.20 - 7.60 (m, aryl-H). Intensity ratio: 2:2:8.

#### b. Polymer synthesis

Poly(p-phenylphenylene vinylene (3): Under inert conditions (argon), 340 mg (1.0 mmol) of 2 and 20 mg of 18-crown-6 ether were dissolved in 50 mL of dry toluene, and a warm solution of 672 mg (6.0 mmol) of potassium-t-butoxide in 50 mL of toluene was added within 2 minutes. After 1 minute, the mixture turned yellow and cloudy. The mixture was heated to reflux for 3 h and cooled to room temperature. Thin layer chromatography control indicated that no monomer or other low-molecular weight substances were present after completion of the reaction. The reaction mixture was filtered to separate a precipitated insoluble product (18%). The filtrate was concentrated to a volume of 30 mL on the rotavap and precipitated with 200 mL of methanol. The precipitated yellow solid was filtered off, washed with methanol and dried. Yield of 3:87 mg

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(49%). The PPPV polymer, 3, showed sufficient solubility in chloroform (max. 0.6 mg/mL). For the characterization and for casting thin films for LEDs, 80 mg of the second fraction of 3 were extracted with 50 mL of chloroform at room temperature for 3 weeks. The insoluble remainder was filtered off. The filtrate showed a concentration of 0.6 mg/mL of 3 and was used for the subsequent characterization and LED fabrication.

Elemental analysis:

10 Calc.: C 94.34% H 5.66% (for monomer unit:  $(C_{14}H_{10})$ )  
Calc.: C 92.23% H 5.52% Br 2.19% (polymer with 40 repeat units)

Found: C 92.07% H 5.80% Br 2.18

15 The elemental analysis revealed that the polymer still contained 2.18% bromine. This indicates an average degree of polymerization of 40 monomeric units under the assumption that all residual bromine atoms are located at the endgroups.

UV (film on glass):  $\lambda_{max} = 425$  nm.

20 IR (KBr): 3022 (w; CH), 1482 (w), 1384 (vs), 958 (w, trans-C=C), 766 (m), 697 (s).

$^1H$  NMR ( $CDCl_3$ ):  $\delta = 6.80 - 7.60$  (m; aryl-H and vinyl-H).

GPC ( $CHCl_3$ ):  $M_n = 6300$  g/mol,  $M_w = 26600$  g/mol (calibrated with polystyrene standards).

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#### B. LED Device Fabrication

The PVK was obtained from Aldrich [catalog #18,260-5] and used as received. As a result of the phenyl side-groups, PPPV is soluble in the conjugated form. A master solution of PPPV in chloroform (stable at room temperature) was prepared. The appropriate amounts were added to a solution of 30 mg PVK in 1 mL chloroform to give PPPV/PVK ratios varying from 1:1000 to 1:10 (weight/weight). To obtain PPPV/PVK films with  
35 concentration 1:10, 1 mL of the chloroform solution

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containing 0.6 mg of PPPV and 6 mg of PVK was concentrated to  $-1/4$  of the original volume just prior to spin casting. Films of the PPPV/PVK blend can be spin-cast from chloroform solution with excellent  
5 reproducibility; the films were light green, homogeneous, dense and uniform.

Recently, electroluminescent devices using a solid state solution of an electron transport small molecule and an emitter molecule dispersed in PVK have  
10 been described (Johnson, G.E. et al., SPIE Symposium on Electronic Imaging: Science & Technology 1910; Electroluminescence: New Materials and Devices for Displays, January 31-February 4, 1993, San Jose, CA). In those experiments, the PVK was doped with a hole  
15 transporting molecule in an attempt to control the hole mobility. By contrast, in this invention, PVK was used as received and without subsequent doping.

The LED structure consists of a calcium rectifying contact on the front surface of a PPPV/PVK  
20 film which has been spin-cast onto a glass substrate partially coated with a layer of indium/tin-oxide (ITO) as the hole-injecting contact (see Fig. 10 for a schematic diagram). The luminescent thin film layers were prepared by spin-casting the blends from chloroform  
25 solution. To determine the optimum concentration of PPPV in PVK, the PPPV/PVK ratio was varied from 1:1000 to 1:10 (weight/weight). The resulting light green polyblend films had uniform surfaces with thicknesses in the range from 1000Å to 3000Å, depending on details (concentration  
30 of solution, spin rate, etc.). Electron-injecting calcium contacts were deposited onto the surface of the blend by vacuum evaporation at pressures below  $4 \times 10^{-7}$  Torr, yielding active areas of 0.1 cm<sup>2</sup>. All processing steps were carried out in a nitrogen atmosphere. Indium  
35 solder was used to connect wires to the electrodes.

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Spectroscopic measurements used a single-grating monochromator (Spex 340S) with a Photometrics CCD camera (Tektronix TK512 CCD) as a detector without correction for system response. Electroluminescence (EL) spectra were recorded while applying direct current. For photoluminescence (PL) spectra, the polymer was excited with ultraviolet light at 365 nm (254 nm was used for obtaining PL spectra of PVK).

The optical absorption spectra of PPPV, PVK and PPPV/PVK (1/10) thin films are shown in Fig. 2. The onset of the  $\pi$ - $\pi^*$  transition of poly(p-phenylene vinylene) (PPV) was at about 500 nm at room temperature. The addition of phenyl groups to the benzene ring did not shift the absorption edge of PPV; the onset of  $\pi$ - $\pi^*$  absorption in PPPV also occurred at around 500 nm, and the absorption peak is at 425 nm. The onset of absorption in PVK was at approximately 355 nm at room temperature; PVK exhibits two well-defined spectral features at 343 and 330 nm, respectively. The highest PPPV/PVK ratio we reached was 1/10, limited by the solubility of PPPV. The PPPV/PVK (1/10) blend had two absorption peaks at 343 and 330 nm, the same as PVK and a shoulder around 418 nm, attributed to PPPV. The blue shift of the  $\pi$ - $\pi^*$  transition of PPPV in PVK resulted in the blue luminescence and electroluminescence which are highly desired.

The forward bias current was obtained when the ITO electrode was positively biased and the Ca electrode grounded. Fig. 3A shows the current vs. voltage characteristics measured from a typical Ca/polyblend(1/50)/ITO device. The forward current increased with increasing forward bias voltage, and the reverse bias current remained small; the rectification ratio was approximately  $10^2 - 10^3$ . Figure 3B shows the voltage dependence of emission intensity from the same

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Ca/polyblend(1/50)/ITO device. Light emission first became visible at a bias of just under 32 V and a current density of approximately 1.7 mA/cm<sup>2</sup>. Above 35 V, blue light emission was visible in the normal room light of the laboratory.

Fig. 4 shows the emission efficiency dependence on PPPV content for devices with different PPPV/PVK ratio (w/w). The efficiency increased with increasing PPPV/PVK ratio while the ratio is below 1/50, and then decreased slightly for ratios above 1/50. The quantum efficiencies was as high as 0.16% photons per electron for the devices in which the PPPV/PVK ratio is 1/50; efficiencies of devices with the PPPV/PVK ratio of 1/1000 were 0.01%, an order of magnitude smaller. The efficiencies of devices with a PPPV/PVK ratio of 1/50 were 2 times greater than that of 1/10. To our knowledge, these quantum efficiencies (0.16% photons per electron for the PPPV/PVK LEDs) are the highest reported to date for blue polymer LEDs.

Fig. 5 compares the emission intensity dependence on current for devices with various PPPV/PVK ratios. As is typical of the polymer LED devices, the emission intensity exhibited an approximately linear increase with injected current. The highest emission intensities were obtained from the device with a PPPV/PVK ratio of 1/50. The emission intensities of devices with PPPV/PVK ratios ranging from 1/10 to 1/200 were much higher than those with the 1/500 and 1/1000 ratios.

The emission efficiency is plotted vs. current for devices with different PPPV/PVK ratios in Fig. 6. The efficiencies increase sharply with increasing injected current and then tend to saturate. We have found good device-to-device reproducibility. Depending on the PPPV/PVK ratio, the LED emitted light blue to light purple light at room temperature.

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Fig. 7 compares the room temperature electroluminescence and photoluminescence spectra obtained from a PPPV/PVK (1/50) blend film in a device configuration. The electroluminescence and photoluminescence spectra of the blend are virtually identical, a feature which is quite generally characteristic of polymer LEDs. Thus, the same excitations (presumably neutral bipolaron excitons) are involved in both cases. In photoluminescence, the neutral bipolaron excitons are formed by lattice relaxation following photo-excitation; in the case of electroluminescence, the same species are formed as the intermediate step in the recombination of an electron polaron and a hole polaron. The emission peak of the PL and EL spectra occurs at around 495 nm, blue shifted by about 55 nm with respect to the 550 nm peak of poly(p-phenylphenylene vinylene) reported in the study by Vestweber, H. et al., Adv. Mater. (1992) 4:661. The blue shift in this higher molecular weight material probably results from the chain conformation or aggregation of PPPV in PVK, analogous to the observed blue shift of the  $\pi$ - $\pi^*$  absorption in poly(3-hexylthiophene) on going from the solid state into solution (Hotta, S. et al., Macromolecules (1987) 20:212).

The photoluminescence spectra of PVK, PPPV/PVK blends and PPPV films are shown in Fig. 8. The emission peak of PPPV/PVK (1:50) is at 490 nm, in between PVK which is around 418 nm, and PPPV which is about 512 nm. As the concentration of PPPV in the blends increases, the photoluminescence emission peak shifts slightly to the red, from 483 nm for 1/200 to 490 nm for 1/50, possibly due to aggregation and interactions of PPPV chains in and with the PVK matrix. The same red shift of the emission peak as a function of PPPV concentration has been

-30-

observed in the electroluminescence emission of PPPV/PVK devices (Fig. 9).

In the blend, PVK is believed to serve four functions: 1) High molecular weight PVK helps to form thin, dense and uniform films. Because the solubility of high molecular weight PPPV in chloroform is limited, a thin film cast from saturated PPPV-chloroform is not thick enough to make LEDs. 2) The blue shift of the electroluminescence (with respect to that of pure PPPV) results from either the chain conformation of PPPV in PVK or the details of the aggregation of PPPV in PVK. 3) As a hole transporting polymer, PVK carries charge to the PPPV in the blend film. The turn on voltage of LEDs made with blends of PPPV and poly(methyl methacrylate), an inert and inactive polymer, is much higher than for devices made with the PPPV/PVK polyblends. 4) The dilution effect due to blending helps enhance the probability of radiative recombination.

The latter leads quite naturally to a peak in efficiency as a function of PPPV concentration (consistent with the data shown in Fig. 4); the efficiency will initially increase with the density of luminescent sites and then decrease as excitation quenching becomes important at higher concentrations.

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#### Example 2

The families of luminescent polymers employed in the blends of this invention and their preparation are generally described in the literature. One representative preparation can be found in USSN 07/66290 of Braun and Heeger. This shows the following:

##### A. Preparation of 1-Methoxy-4-(2-Ethyl-Hexyloxy)Benzene

A solution of 24.8 g (0.2 mole) of 4-methoxy phenol in 150 ml dry methanol was mixed under nitrogen

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with 2.5 M solution of sodium methoxide (1.1 equivalent) and refluxed for 20 min. After cooling the reaction mixture to room temperature, a solution of 2-ethylbromohexane (42.5 ml, 1.1 equivalent) in 150 ml methanol was added dropwise. After refluxing for 16 h, the brownish solution turned light yellow. The methanol was evaporated and the remaining mixture of the white solid and yellow oil was combined with 200 ml of ether, washed several times with 10% aqueous sodium hydroxide, H<sub>2</sub>O and dried over MgSO<sub>4</sub>. After the solvent was evaporated, 40 g (85%) of yellow oil was obtained. The crude material was distilled under vacuum (2.2 mm Hg, b.p. 148-149°C), to give a clear, viscous liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.98 (4H, s, aromatics), 3.8 (5H, t, O-CH<sub>2</sub>, O-CH<sub>3</sub>), 0.7-1.7 (15 H, m, C<sub>7</sub>H<sub>15</sub>). IR (NaCl plate) 750, 790, 825, 925, 1045, 1105, 1180, 1235, 1290, 1385, 1445, 1470, 1510, 1595, 1615, 1850, 2030, 2870, 2920, 2960, 3040. MS. Anal. Calc. for C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>: C, 76.23; H, 10.23; O, 13.54. Found: C, 76.38; H, 10.21; O, 13.45.

B. Preparation of 2,5-bis(Chloromethyl)-1-Methoxy-4-(2-Ethyl-Hexyloxy)Benzene

To the solution of 4.9 g (20.7 mmoles) of compound (1) in 100 ml p-dioxane cooled down to 0-5°C, 18 ml of conc. HCl, and 10 ml of 37% aqueous formalin solution was added. Anhydrous HCl was bubbled for 30 min, the reaction mixture warmed up to R.T. and stirred for 1.5-2 h. Another 10 ml of formalin solution was added and HCl gas bubbled for 5-10 min at 0-5°C. After stirring at R.T. for 16 h, and then refluxed for 3-4 h. After cooling and removing the solvents, an off-white "greasy" solid was obtained. The material was dissolved in a minimum amount of hexane and precipitated by adding methanol until the solution became cloudy. After cooling, filtering and washing with cold methanol, 3.4 g

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(52%) of white crystalline material (mp 52-54°C) was obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.98 (2H, s, aromatics), 4.65 (4H, s, CH<sub>2</sub>-Cl), 3.86 (5H, t, O-CH<sub>3</sub>, O-CH<sub>2</sub>), 0.9-1.5 (15H, m, C<sub>7</sub>H<sub>15</sub>), IR (KBr) 610, 700, 740, 875, 915, 1045, 1140, 1185, 1230, 1265, 1320, 1420, 1470, 1520, 1620, 1730, 2880, 2930, 2960, 3050. MS. Anal. Calc. for C<sub>17</sub>H<sub>26</sub>O<sub>2</sub>Cl<sub>2</sub>: C, 61.26; H, 7.86; O, 9.60; Cl, 21.27. Found: C, 61.31; H, 7.74; O, 9.72; Cl, 21.39.

5  
10 C. Preparation of Poly(1-Methoxy-4-(2-Ethylhexyloxy-2,5-Phenylenevinylene) MEH-MPV

To a solution of 1.0 g (3 mmol) of 2,5-bis(chloromethyl)-methoxy-4-(2-ethylhexyloxy)benzene in 20 ml of anhydrous THF was added dropwise a solution of 2.12 g (18 mmol) of 95% potassium tert-butoxide in 80 ml of anhydrous THF at R.T. with stirring. The reaction mixture was stirred at ambient temperature for 24 h and poured into 500 ml of methanol with stirring. The resulting red precipitate was washed with distilled water and reprecipitated from THF/methanol and dried under vacuum to afford 0.35 g (45% yield). UV (CHCl<sub>3</sub>) 500. IR (film) 695, 850, 960, 1035, 1200, 1250, 1350, 1410, 1460, 1500, 2840, 2900, 2940, 3040. Anal. Calc. for C<sub>17</sub>H<sub>24</sub>O<sub>2</sub>: C, 78.46; H, 9.23. Found: C, 78.34; H, 9.26.

Molecular weight (GPC vs. polystyrene) 3 x 10<sup>5</sup>.  
25 Inherent viscosity - 5 dl/g (but time dependent due to the tendency to form aggregates). As is the case with a few other stiff chain polymers, the viscosity increases with standing, particularly in benzene. The resulting solution is therefore thixotropic.

30 D. Polymerization of the Precursor Polymer and Conversion to MEH-PPV

A solution of 200 mg (0.39 mmol) of the monomer salt in 1.2 ml dry methanol was cooled to 0°C for 10 min and a cold degassed solution of 28 mg (1.7 equivalents)

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of sodium hydroxide in 0.7 ml methanol was added slowly. After 10 min the reaction mixture became yellow and viscous. The above mixture was maintained at 0°C for another 2-3 h and then the solution was neutralized. A  
5 very thick, gum-like material was transferred into a Spectrapore membrane (MW cutoff 12,000-14,000) and dialyzed in degassed methanol containing 1% water for 3 days. After drying in vacuo, 70 mg (47%) of "plastic" yellow precursor polymer material was obtained. UV  
10 (CHCl<sub>3</sub>) 365. IR (film) 740, 805, 870, 1045, 1075, 1100, 1125, 1210, 1270, 1420, 1470, 1510, 2930, 2970, 3020. Soluble in C<sub>6</sub>H<sub>5</sub>Cl, C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, Et<sub>2</sub>O, THF. Insoluble in MeOH.

The precursor polymer was converted to the  
15 conjugated MEH-PPV by heating to reflux (approx. 214°C) in 1,2,4-trichlorobenzene solvent.

This material can be blended with a suitable fraction of hole transporting polymer and used as a solution to form an active layer in LEDs.

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We Claim:

1. A light emitting polymer composition comprising
  - a) a hole transporting polymer and
  - b) a polymeric conjugated organic emitterhaving at least two mer units in intimate blended admixture.
2. The light emitting polymer composition of claim 1 wherein the weight ratio of the hole transporting polymer to the polymeric conjugated organic emitter is greater than about 2:1.
3. The light emitting polymer composition of claim 1 wherein the weight ratio of the hole transporting polymer to the polymeric conjugated organic emitter is from about 2:1 to about 2000:1.
4. The light emitting polymer composition of claim 3 wherein the polymeric conjugated organic emitter is a  $\pi$ -conjugated polymer which has at least three mer units.
5. The light emitting polymer composition of claim 3 wherein the hole transporting polymer is a carbazole group containing polymer.
6. The light emitting polymer composition of claim 3 wherein the hole transporting polymer is an aromatic amine group containing polymer.

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7. The light emitting polymer composition of claim 3 wherein the hole transporting polymer has a nonconjugated organic backbone with hole carrying conjugated groups pendant from it.

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8. The light emitting polymer composition of claim 7 wherein the nonconjugated backbone is a carbon-containing backbone.

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9. The light emitting polymer composition of claim 7 wherein the nonconjugated backbone is a silicon-containing backbone.

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10. The light emitting polymer composition of claim 5 wherein the conjugated groups are carbazole groups.

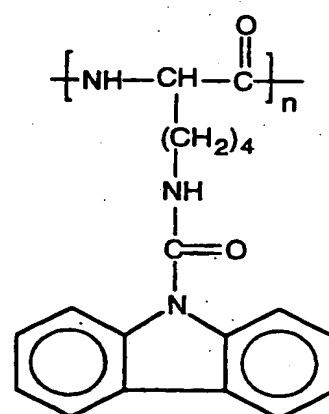
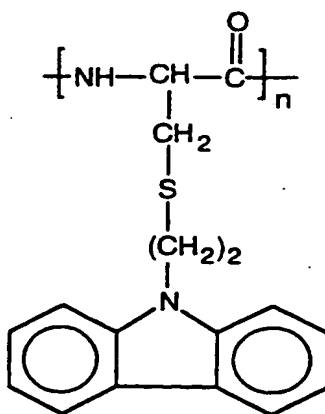
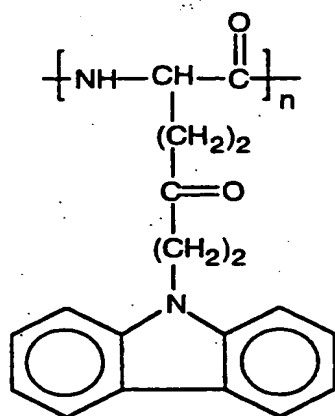
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11. The light emitting polymer composition of claim 8 wherein the conjugated groups are carbazole groups and the hole transporting polymer has a formula selected from the group consisting of

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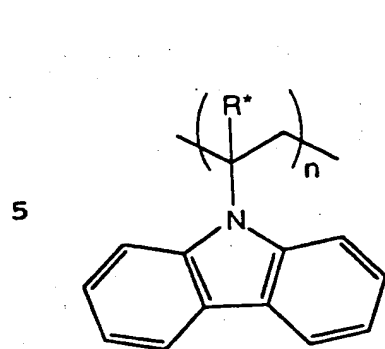
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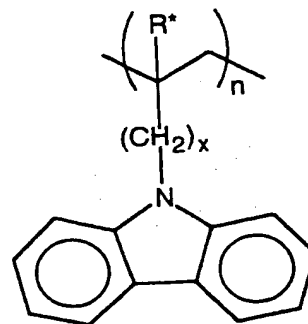
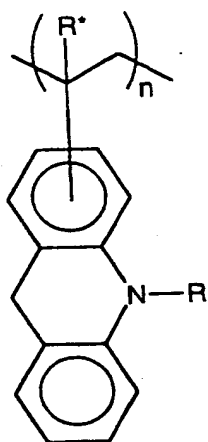


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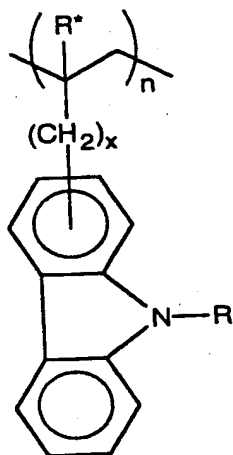
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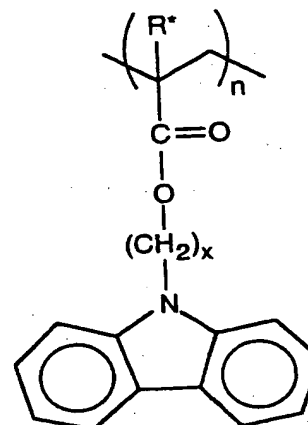
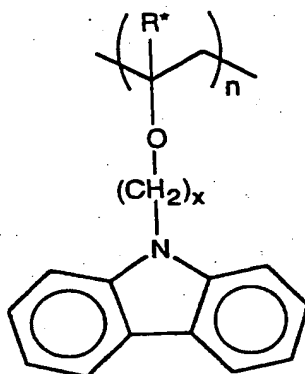
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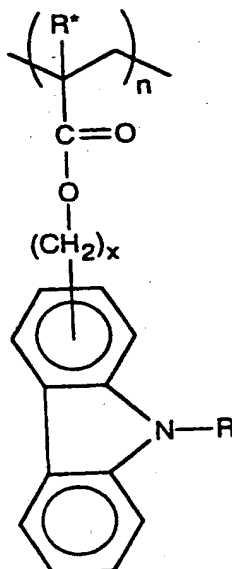
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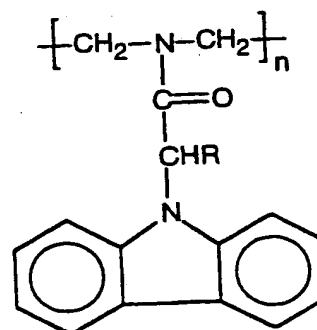


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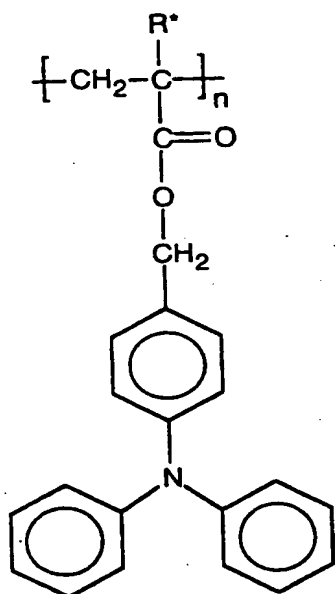
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in which n is an integer greater than 1, x is an integer of from 1 to about 15 inclusive, x' is an integer of from 1 to about 8 inclusive, R' is hydrogen or alkyl, and R is alkyl.

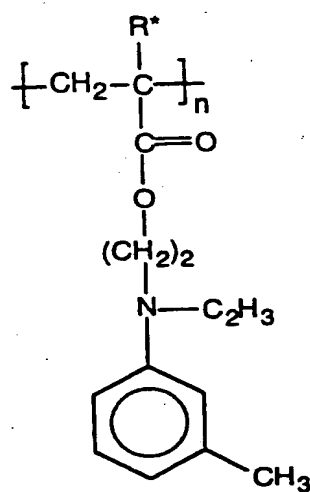
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12. The light emitting polymer composition of claim 8 wherein the hole transporting polymer has a formula selected from the group consisting of

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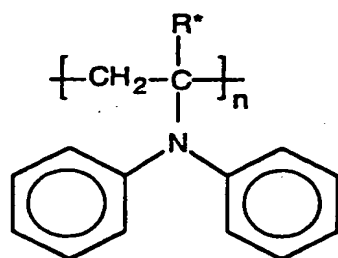


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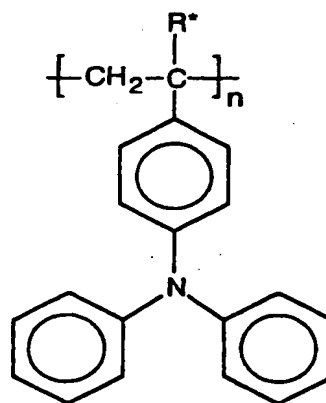


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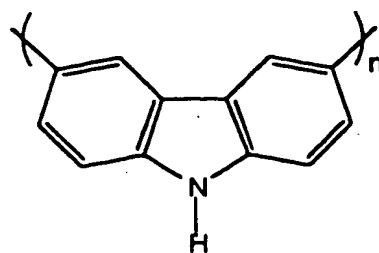
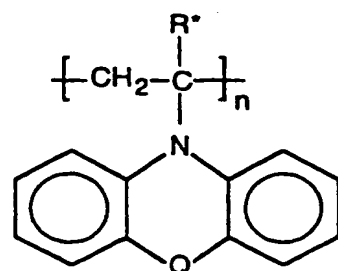
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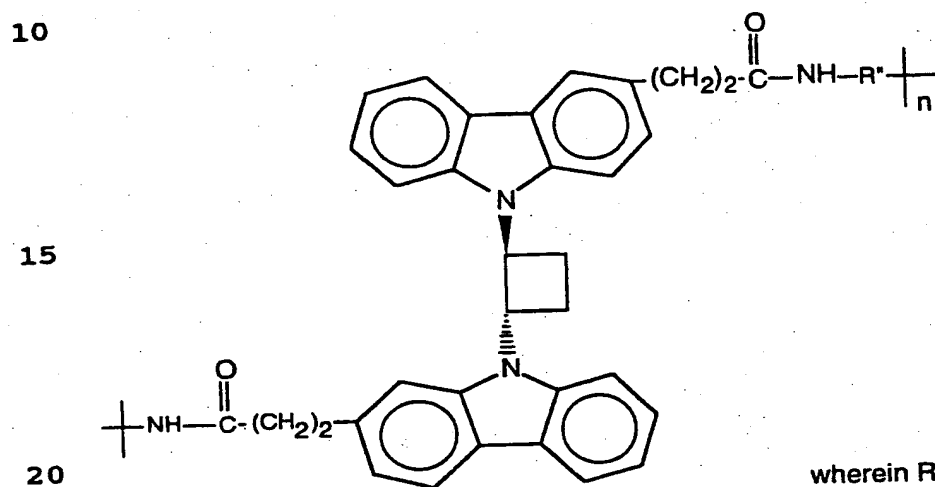
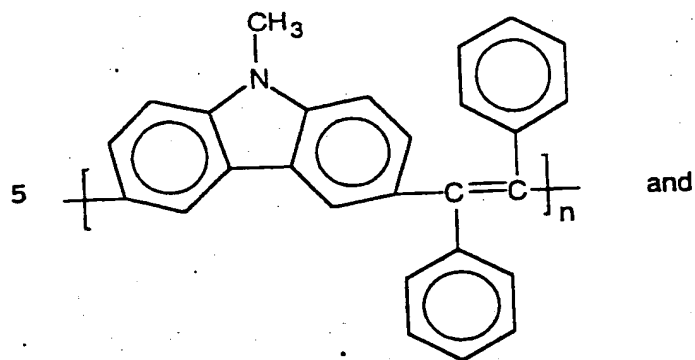


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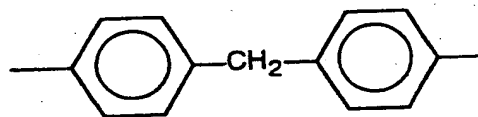
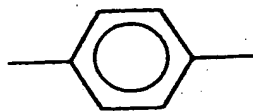


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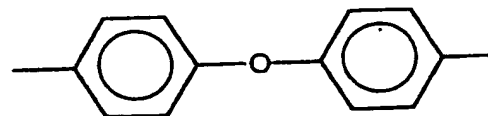
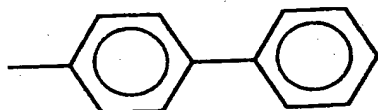
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wherein R<sup>n</sup> is

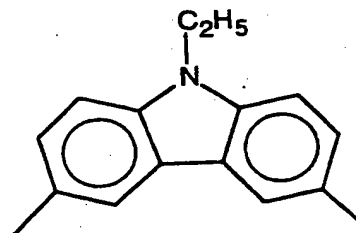
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or



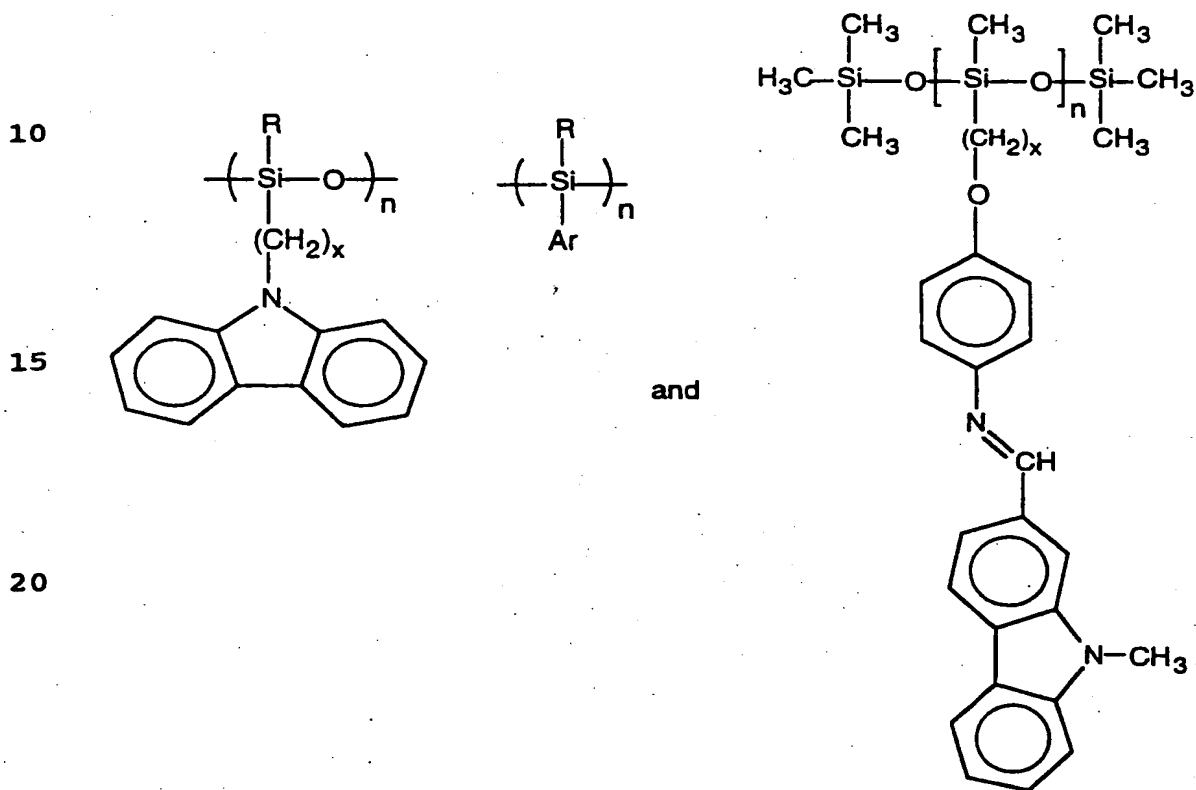
35 n is an integer greater than 1, Q is S or O, and R<sup>n</sup> is hydrogen or alkyl.



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13. The light emitting polymer composition of claim 8 wherein the hole transporting polymer is PVK.

14. The light emitting polymer composition of claim 3 wherein the hole transporting polymer has a formula selected from the group consisting of



in which  $n$  is an integer greater than 1,  $x$  is an integer of from 1 to about 15 inclusive,  $Ar$  is an aromatic group of from 6 to about 12 carbons,  $R$  is alkyl.

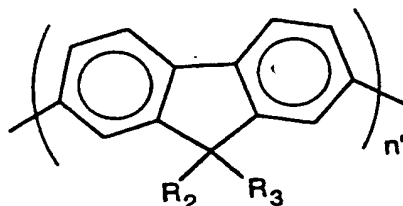
15. The light emitting polymer composition of claim 3 wherein the hole transporting polymer is a polymer having a backbone which includes a series of discontinuous conjugated groups isolated from one another by nonconjugated regions.

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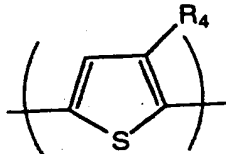
16. The light emitting polymer composition of claim 15 wherein the conjugated groups are olefinic and/or aromatic groups.

17. The light emitting polymer composition of claim 15 wherein the nonconjugated regions are carbonate linkages.

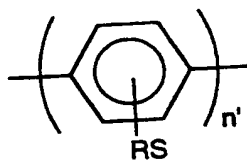
18. The light emitting polymer composition of claim 4 wherein the polymeric conjugated emitter is selected from the group consisting of polyfluorenes of the formula



poly(thiophenes) represented by the formula

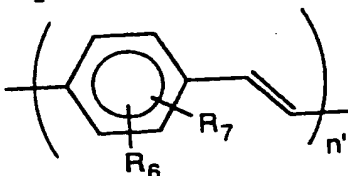


poly(p-phenylenes) represented by the formula



and

poly(phenylene vinylenes) represented by the formula



wherein  $n'$  is at least 2,  $R_2$ ,  $R_3$  and  $R_4$  are each independently selected from hydrogen and alkyls of from 1 to 16 carbon atoms,  $R_5$  is selected from hydrogen, an alkyl having from 1 to about 12 carbons and an aromatic

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group of from about 6 to about 12 carbons, and R6 and R7 are each independently selected from hydrogen, an alkyl having from 1 to about 12 carbons, an aromatic group of from about 6 to about 12 carbons and an alkoxyl having from 1 to about 25 carbons.

19. The light emitting polymer composition of claim 18 wherein the polymeric conjugated emitter is selected from the group consisting of poly(p-phenylphenylene vinylene) ("PPPV"), poly(p-phenylene vinylene) ("PPV"), poly(2,5-dimethoxyphenylene vinylene) ("PDMPV"), poly(2-methoxy,5-ethylhexyloxyphenylene vinylene) ("MEH-PPV"), and poly(2-methoxy,5-(2'-ethylhexyloxy)-p-phenylene vinylene) ("PCHA-PPV").

15

20. The light emitting polymer composition of claim 19 wherein the polymeric conjugated organic emitter is PPPV.

20

21. The light emitting polymer composition of claim 1 comprising 5 to 1000 parts by weight of PVK and 1 part by weight of PPPV.

25

22. In a light emitting diode comprising a transparent conducting first layer having a high work function and serving as a ohmic hole-injecting electrode,

30

- a film of light-producing conjugated polymer present upon said conducting first layer, and a negative, electron-injecting contact formed from a low work function metal and present upon said film of light-producing conjugated polymer so as to act as a rectifying contact in the diode structure,

35

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the improvement which comprises  
employing as said film of light-producing  
conjugated polymer a film of polymer composition  
comprising

- 5           a) a hole transporting polymer and  
          b) a polymeric conjugated organic emitter  
having at least two mer units  
in intimate blended admixture.

10           23. The light emitting diode of claim 22  
wherein the weight ratio of the hole transporting polymer  
to the polymeric conjugated organic emitter is greater  
than about 2:1.

15           24. The light emitting diode of claim 22  
wherein the polymer composition comprises  
5 to 1000 parts by weight of PVK and 1 part by  
weight of PPPV.

20           25. A light emitting diode comprising  
a transparent conducting first layer having a  
high work function and serving as a ohmic hole-injecting  
electrode,

          a film of light-producing conjugated polymer  
25   blend comprising

- a) a hole transporting polymer and  
          b) a polymeric conjugated organic emitter  
having at least two mer units  
in intimate admixture.

30   present upon said conducting first layer, and  
          a negative, electron-injecting contact formed  
from a low work function metal and present upon said film  
of light-producing conjugated polymer so as to act as a  
rectifying contact in the diode structure.

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26. A casting solution for forming an active layer in a light emitting diode comprising  
a solvent having dissolved therein  
a) a hole transporting polymer and  
5 b) a polymeric conjugated organic emitter  
having at least two mer units.

10

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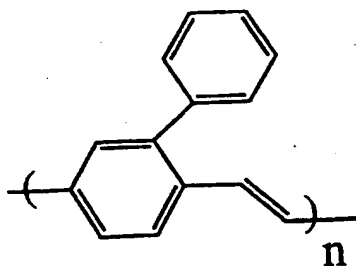
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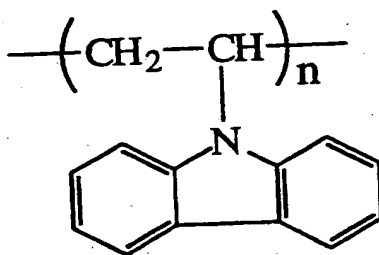
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PPPV

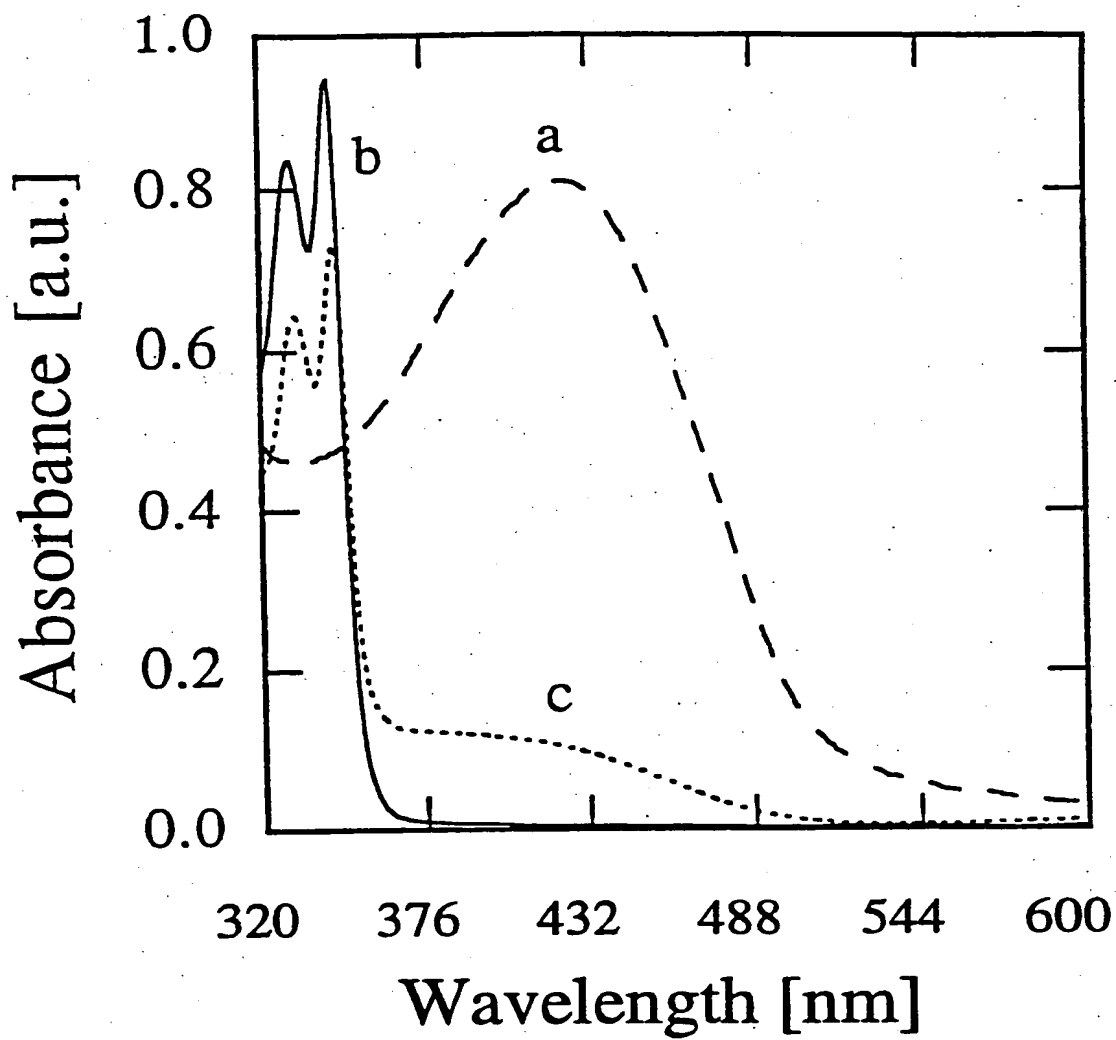
FIG. 1A



PVK

FIG. 1B

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**FIG. 2**

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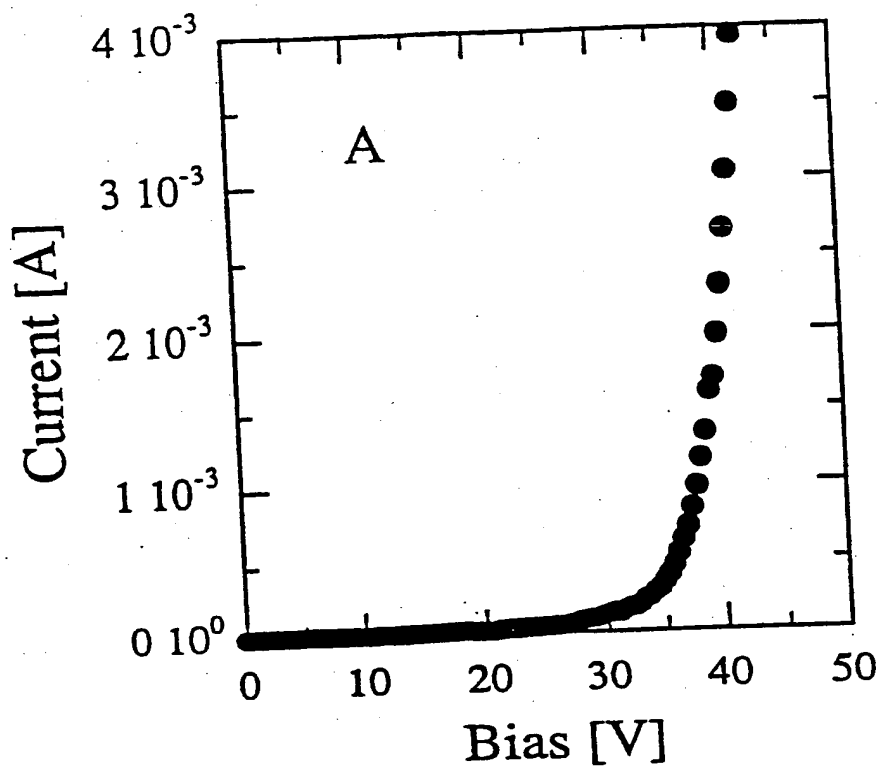


FIG. 3A

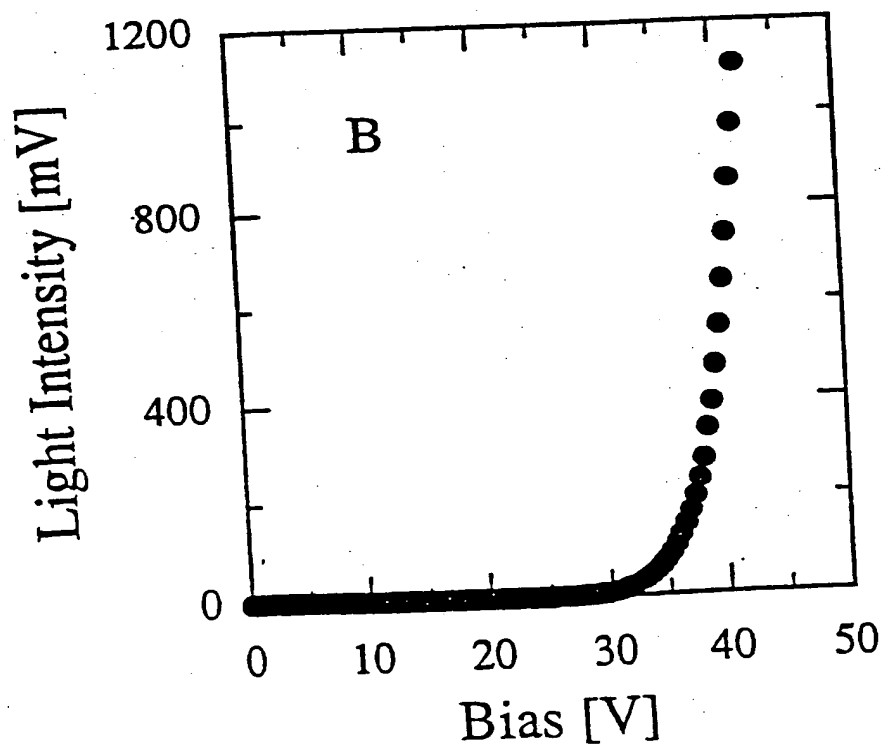


FIG. 3B

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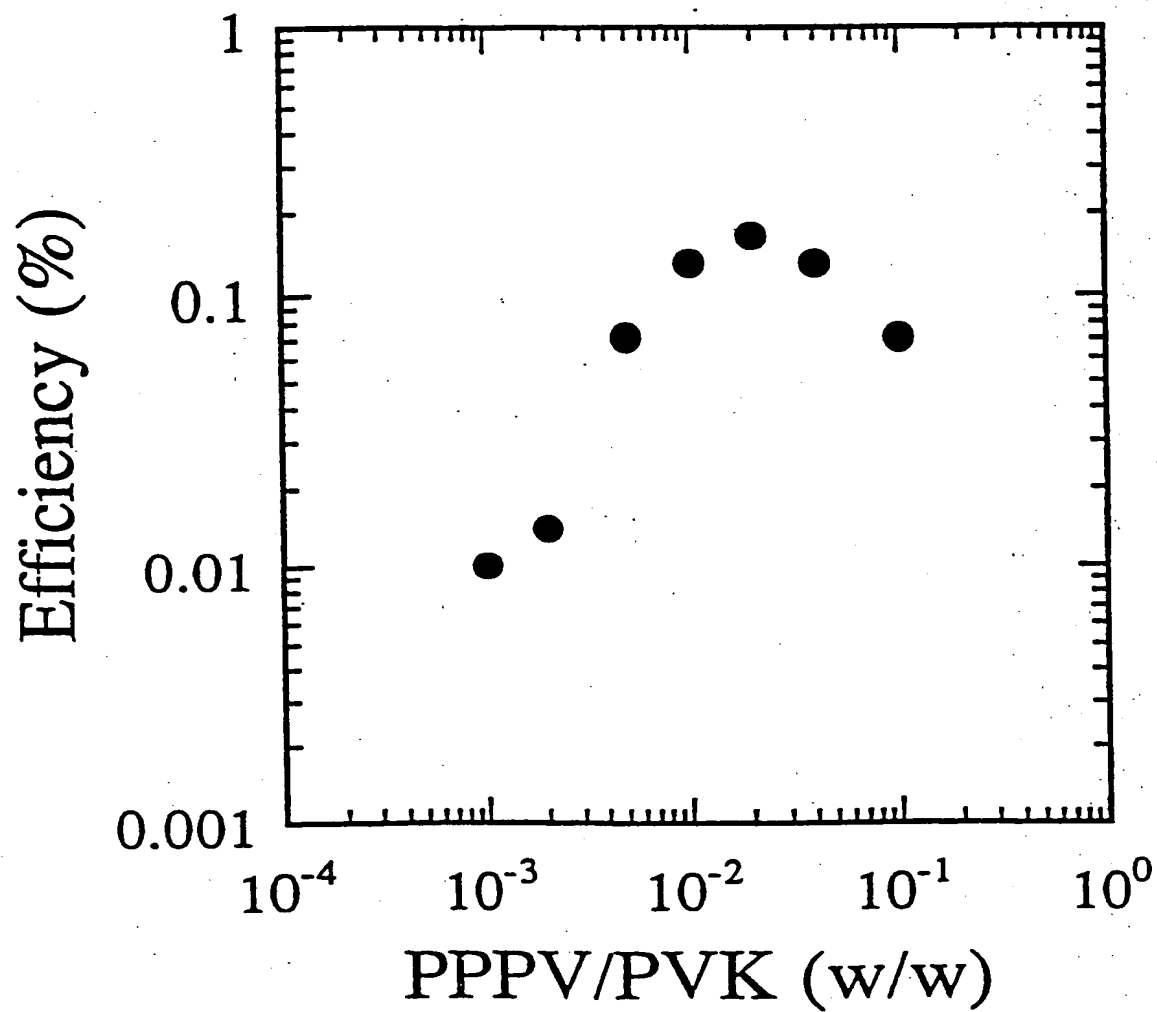


FIG. 4

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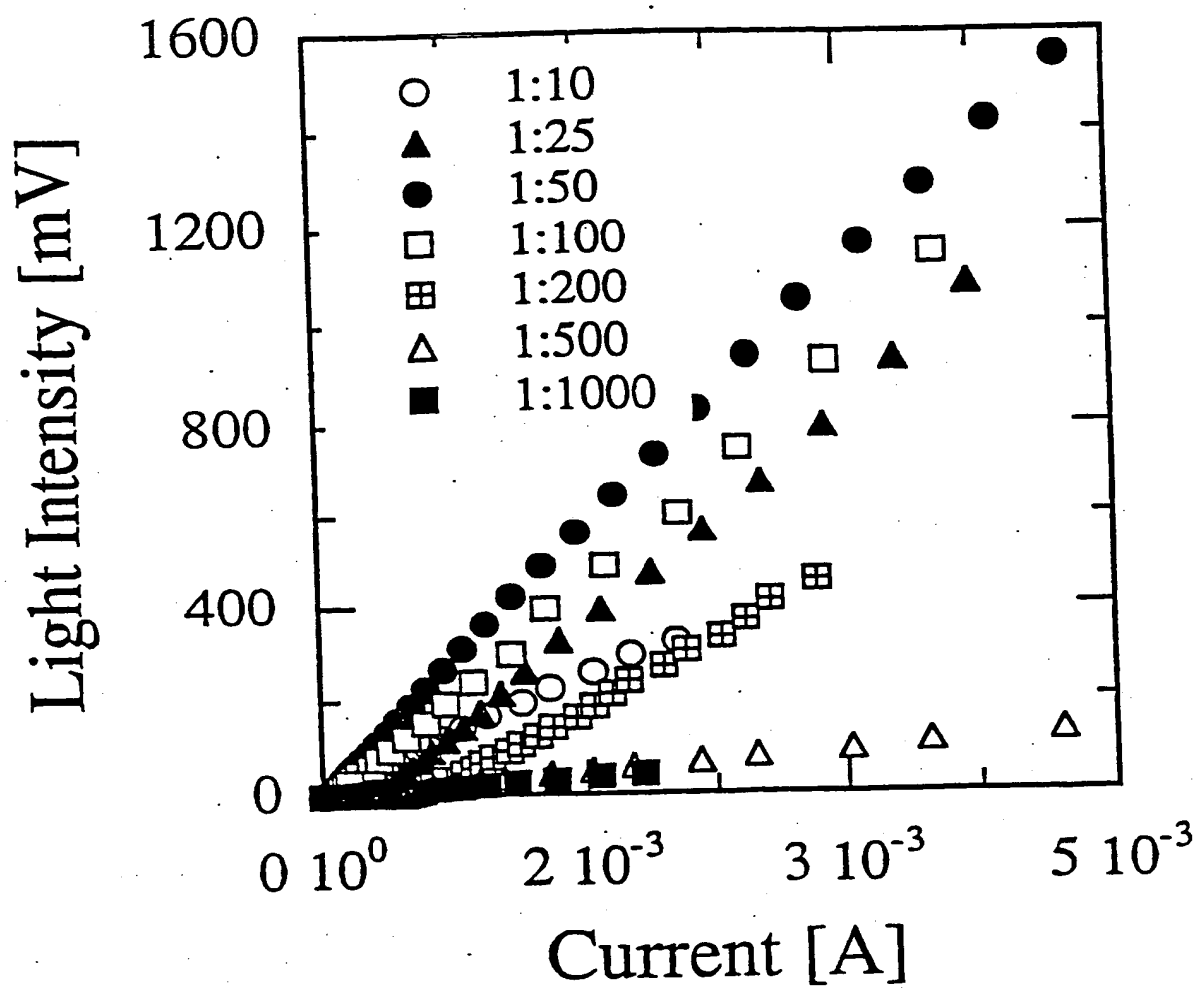


FIG. 5

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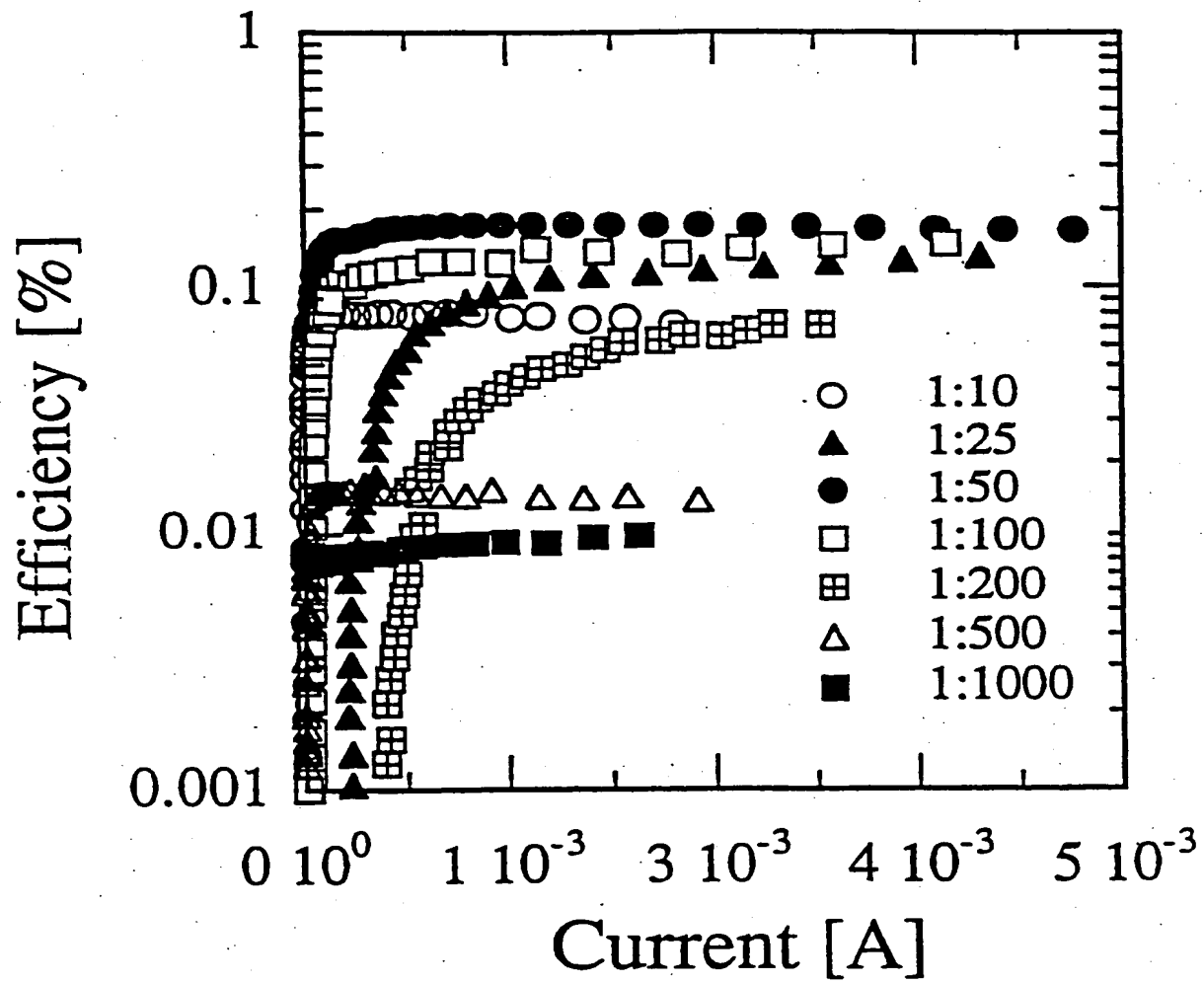
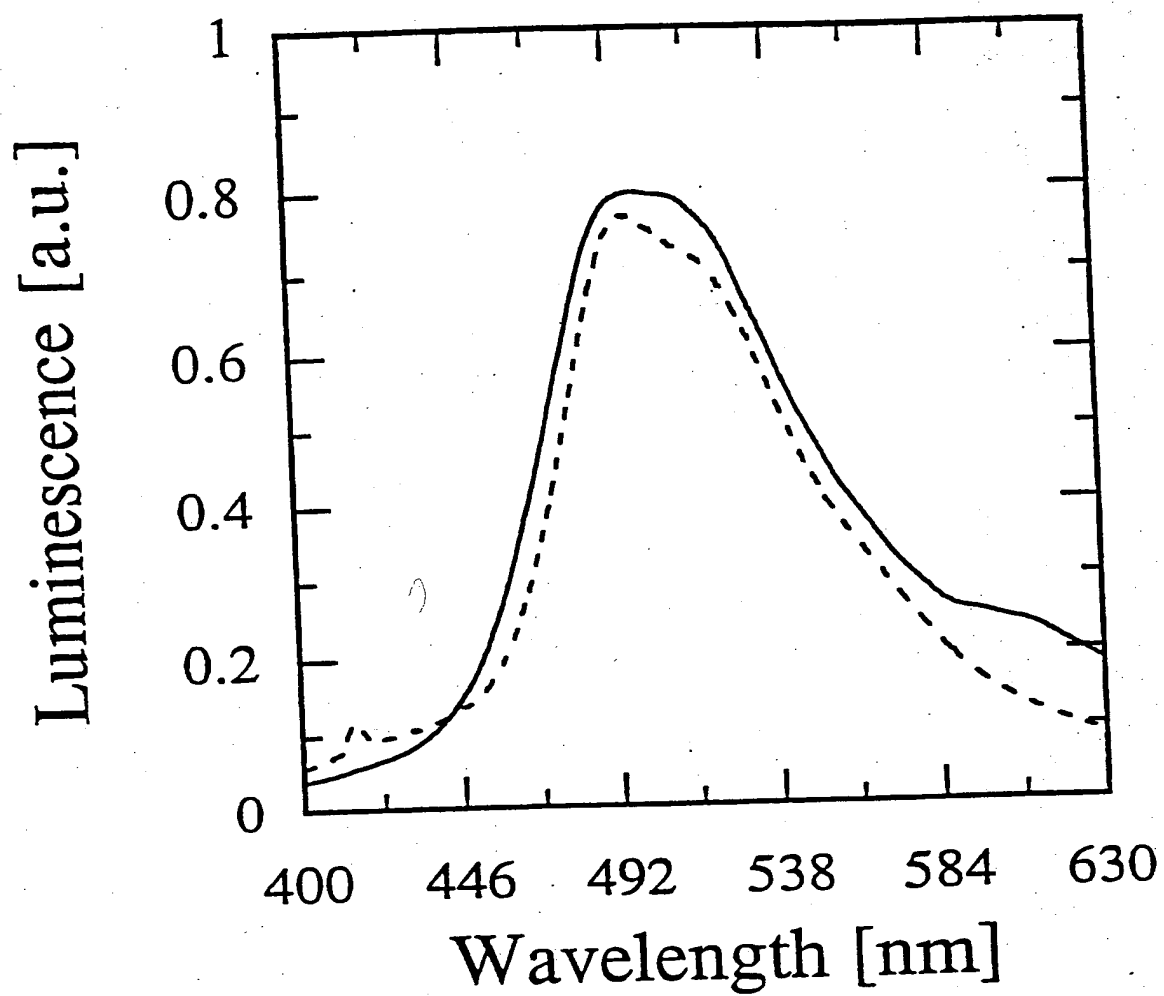


FIG. 6

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**FIG. 7**

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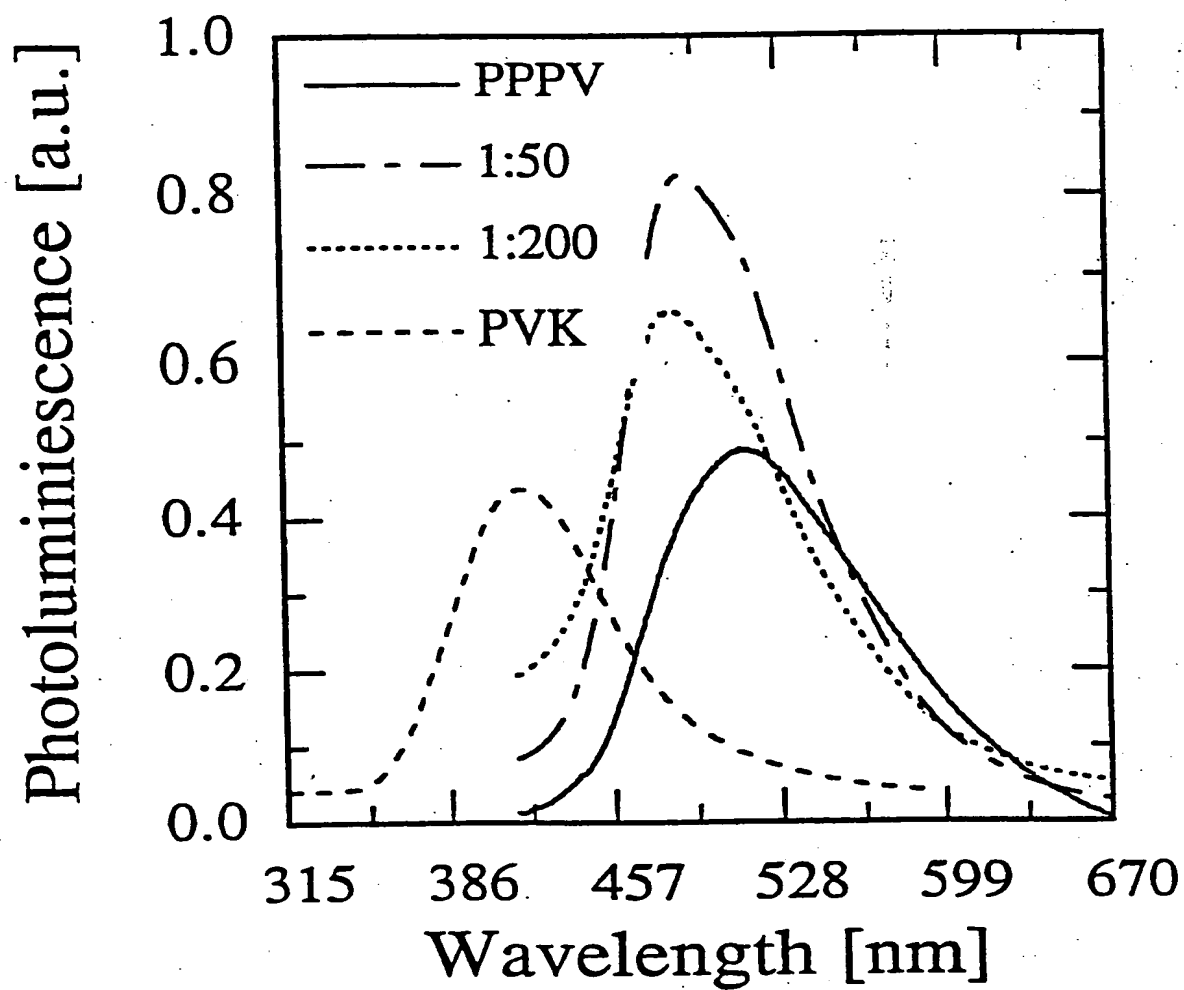


FIG. 8

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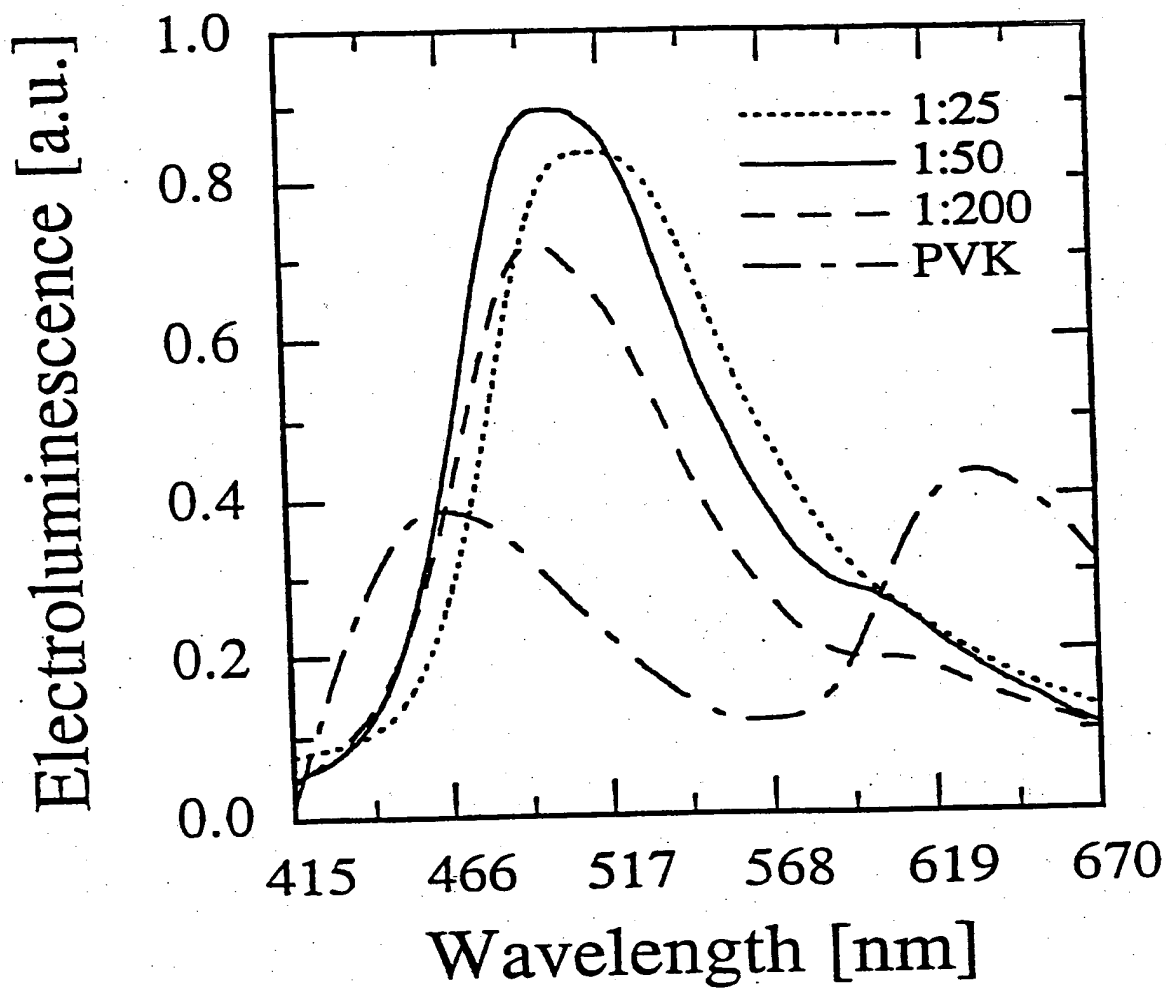
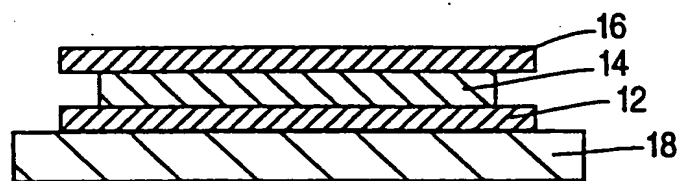


FIG. 9

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**FIG. 10**

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/07649

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 15/04; C08G 63/48, 63/91

US CL :428/457; 525/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/457; 525/50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, P	US, A, 5,247,190 (FRIEND ET AL.) 21 September 1993, see abstract.	1-26
A, E	US, A, 5,334,539 (SHINAR ET AL.) 02 August 1994, see abstract.	1-26

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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